Electronic Supplementary Information
for
Unlocking Lewis Acidity *via* the Redox Non-Innocence of a Phenothiazine-Substituted Borane

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S1. General Considerations

All reactions were carried out under an atmosphere of anhydrous N_2 using standard glovebox (MBraun LABstar) and/or Schlenk techniques unless otherwise stated. All glassware, needles, and stir bars were dried in an oven at 140 °C and/or flame dried under vacuum before use. All solvents were obtained from an MBraun MB-SPS 800 solvent purification system, collected under vacuum, and dried over 4Å molecular sieves prior to use. All commercially available reagents were used as received from Sigma Aldrich, TCI Chemicals, or Oakwood Chemicals and used without further purification. Bis(pentafluorophenyl)phenothiazylborane,[1] bismesityl-phenothiazylborane,[2] (4-bromophenyl)dimesitylborane[3] and (10-phenylphenothiazinyl)-dimesitylborane[4] were synthesized following known literature procedures. Deuterated solvents were degassed by employing a freeze-pump-thaw procedure and dried over 4Å molecular sieves before use.

S1.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

Spectra were acquired on either DRX 600 MHz, Bruker Avance NEO 400 MHz, or Bruker Avance NEO 300 MHz NMR spectrometers at 25 °C and referenced to the corresponding residual solvent peak of deuterated solvent (chloroform-d or acetonitrile-d_3). Chemical shifts for protons (^{1}H) and carbons (^{13}C) are reported relative to tetramethylsilane ($SiMe_4$). Chemical shifts for fluorine (^{19}F) and boron (^{11}B) are reported relative to 15 % BF_3-Et_2O. The NEO systems were operated using Topspin version 4.0.8 and the DRX system was operated using Xwinnmr version 3.5 and analyzed using Mestrenova 14.3.1 software. Chemical shifts are reported in ppm, coupling constants reported in hertz (Hz), and conventional abbreviations for multiplicity were used (br = broad, s = singlet, d = doublet, t = triplet, dt = doublet of triplets, m = multiplet). All percent conversions in catalytic reactions were calculated using NMR integration.

S1.2 Cyclic Voltammetry

Cyclic voltammetry measurements were performed using a AUTOLAB PGSTAT204 potentiostat equipped with a typical three-electrode cell with a Pt wire counter electrode, an Ag/AgCl reference electrode and glassy carbon working electrode. Measurements were performed at room temperature in dry, degassed dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$). The scan rate was 100 mV/s and the current was 100 μA.

S1.3 Electron Paramagnetic Resonance (EPR) Spectroscopy

X-band continuous-wave EPR (cw-EPR) spectra were collected at room temperature using a Bruker X-band CW Magnettech ESR5000 spectrometer. EPR data was collected in solution with $\mathbf{3}^{\bullet+}$ dissolved in 0.4 mL of either CH_2Cl_2 or acetonitrile and 0.1 mL was dispensed into a 3 mm quartz EPR tube.

S1.3 Mass Spectrometry

Mass spectrometry data was provided from the AIMS Mass Spectrometry Laboratory at the University of Toronto and was acquired using dual electrospray ionization in positive mode on an Agilent 6538 UHD instrument.

S1.4 X-ray Crystallographic Methods

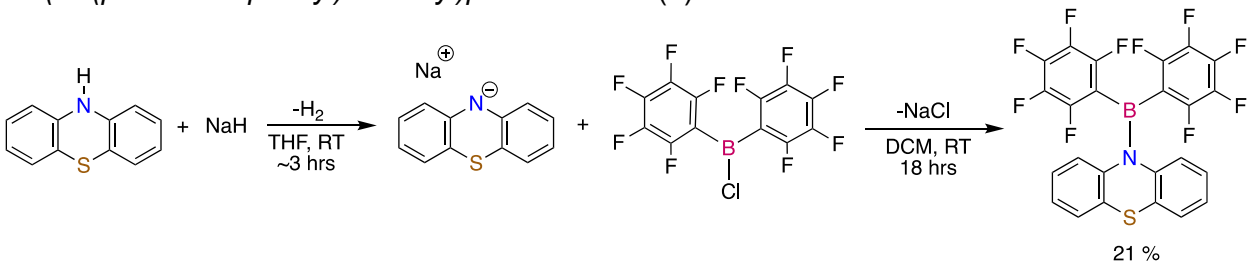
Crystals suitable for X-ray diffraction were grown from the slow evaporation of pentane into a CH_2Cl_2. Crystals were chosen under paratone oil and mounted to the diffractometer under a stream of N_2 and kept at 173.0 K or 150.0 K during data collection. Diffraction data was collected

on a Bruker APEX-II CCD diffractometer with a MoK_{α} (λ = 0.71073) radiation source. Using Olex2,[5] the structure was solved with the XS structure solution program using Direct Methods and refined with the SHELXL refinement package[6] using Least Squares minimization. Images were generated using ORTEP.

S2 Synthetic Procedures and Characterization

S2.1 Synthesis and Characterization of 1, 2, and 3

10-(bis(pentafluorophenyl)boraneyl)phenothiazine (**1**):[1]



Phenothiazine (0.115 g, 0.578 mmol, 1 eq.) was dissolved in approximately 3 mL of tetrahydrofuran (THF). Sodium hydride (0.016 g, 0.636 mmol, 1.1 eq.) was suspended in THF and added dropwise to the phenothiazine solution. The resulting mixture was allowed to stir until the evolution of gas stops. The solvent was removed in vacuo to yield a yellow sodium amide precipitate, which was resuspended in CH_2Cl_2. A solution of chlorobis(pentafluorophenyl)borane (0.2199 g, 0.578 mmol, 1 eq.) was prepared in approximately 2 mL of CH_2Cl_2. The yellow sodium amide salt suspension was added dropwise to the chlorobis(pentafluorophenyl)borane solution and left stirring overnight at room temperature. The solvent was removed in vacuo to yield a brown oil. The aminoborane product was solidified by washing three times with pentanes and drying in vacuo to yield a beige solid (0.150 g, 48 %). NMR resonances are consistent with previous literature reports.

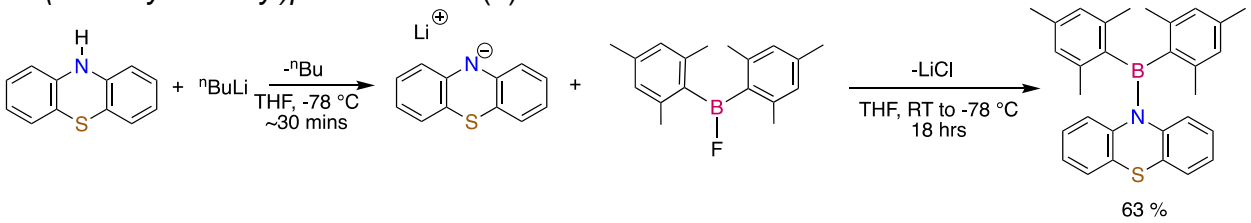
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (dd, 2H, *J* = 8.1, 1.5 Hz), 7.17 (td, 4H, *J* = 7.7, 1.3 Hz, 4H), 7.09 (m, 2H).

^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$) δ: 130.17 (m, 4F), -151.83 (t, 2F, *J* = 20.1 Hz), -160.97 (m, 4F).

^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$) δ: 38.6 (br).

^{13}C {^{1}H} NMR (101 MHz, CDCl3) δ: 145.9 (d, *J* = 243.8 Hz), 142.0, 141.9 (d, *J* = 256.9 Hz), 137.3 (d, *J* = 252.3 Hz), 132.5, 128.1, 127.2, 127.1, 124.1, 111.0.

10-(dimesitylboraneyl)phenothiazine (**2**):[2]



63 %

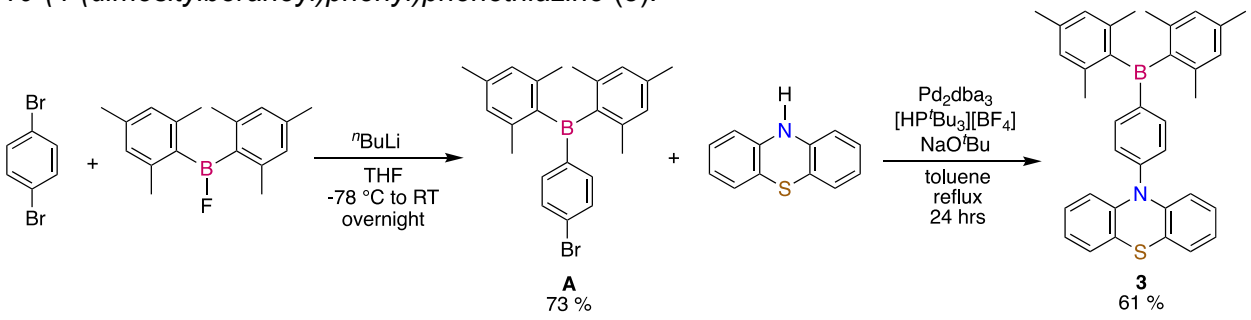
Phenothiazine (0.794 g, 4 mmol) was dissolved in 40 mL of anhydrous tetrahydrofuran (THF) and cooled to -78 °C. *n*-Butyllithium (*n*-BuLi) (2.625 mL, 1.6 M in hexanes, 4.2 mmol) was added dropwise, and the resulting yellow solution was stirred for 30 minutes. Separately, dimesitylfluoroborane (1.126 g, 4.2 mmol) was dissolved in 8 mL of THF. This solution was added dropwise to the yellow solution at -78 °C. The mixture was allowed to stir and warm to room temperature overnight. The solvent was removed in vacuo, resulting in an off-white solid which was extracted with dichloromethane (CH_2Cl_2) and washed with brine. The solution was dried with $MgSO_4$ and filtered before the solvent was removed in vacuo, yielding a pale blue solid. The product was purified using flash column chromatography with hexanes as an eluent. The solvent was removed under reduced pressure and in vacuo to give the white product (1.125 g, 63 % yield). NMR resonances are consistent with previous literature reports.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27-7.24 (m, 2H) 7.17-7.14 (m, 2H), 7.01-6.97 (m, 2H), 6.89-6.87 (m, 2H), 6.66 (s, 4H), 2.37 (s, 12H), 2.18 (s, 6H).

^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$) δ: 51.0.

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ: 143.6, 140.7, 137.2, 129.9, 128.1, 127.2, 126.5, 125.5, 125.3, 24.1, 21.1.

10-(4-(dimesitylboraneyl)phenyl)phenothiazine (**3**):[3,4]



A solution of *para*-dibromobenzene (0.440 g, 1.864 mmol, 2 eq.) was prepared in anhydrous THF (10 mL) and cooled to -78 °C in a dry ice/acetone bath. To the cooled solution, 2.5 M ^{n}BuLi in hexanes (0.78 mL, 1.864 mmol, 2 eq.) was added dropwise over 20 minutes and the solution was stirred at -78 °C for 1 hour. Dimesitylfluoroborane (0.250 g, 0.932 mmol, 1 eq.) was dissolved in anhydrous THF and transferred to an addition funnel before being added dropwise to the previous solution at -78 °C. The solution was stirred at -78 °C for 1 hour before being allowed to warm to room temperature while stirring overnight. Distilled water (5 mL) was added to quench the reaction and the mixture was extracted with CH_2Cl_2, washed with distilled water, and dried over sodium sulfate. The crude material was filtered before purification by column chromatography using hexanes as eluent. The product **A** was isolated as a white solid (0.1021 g, 73 % yield).

Under an inert atmosphere, a 50 mL Schlenk flask was charged with a 15 mL anhydrous toluene solution of **A** (0.276 g, 0.680 mmol, 1 eq.), phenothiazine (0.136 g, 0.680 mmol, 1 eq.), Pd_2dba_3 (0.028 g, 0.020 mmol, 0.03 eq.), tri-*tert*-butylphosphonium tetrafluoroborate (0.010 g, 0.034 mmol, 0.05 eq.), and sodium *tert*-butoxide (0.131 g, 1.360 mmol, 2 eq.). The flask was equipped with a reflux condenser and heated to reflux under nitrogen for 24 hours. The reaction was quenched with 10 mL of distilled water and extracted with dichloromethane. The organic layer was dried over sodium sulfate and purified by column chromatography using hexanes/CH_2Cl_2 (5:1 v/v). The product was isolated as a bright yellow solid (0.217 g, 61 % yield). NMR resonances are consistent with previous literature reports.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.56 (d, 2H, *J* = 8.4 Hz), 7.22 (d, 2H, *J* = 8.4 Hz), 7.18 (dd, 2H, *J* = 7.4, 1.8 Hz), 7.07-6.90 (m, 4H), 6.82 (s, 4H), 6.68 (dd, 2H, *J* = 8.0, 1.4 Hz), 2.30 (s, 6H), 2.05 (s, 9H)

^{11}B {^{1}H} NMR (128 MHz, $CDCl_3$) δ: 74.5.

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ: 146.0, 143.1, 142.9, 141.8, 140.9, 138.9, 138.8, 128.4, 127.7, 127.1, 125.8, 124.2, 124.0, 120.4, 23.7, 21.4.

S2.2 Single-electron Oxidation of 1, 2, and 3

General procedure for single-electron oxidation: A suspension of oxidant (1.0 eq.) in 0.5 mL of dichloromethane (CH_2Cl_2) was added dropwise using a Pasteur pipette to a solution of **1**, **2**, or **3** (1.0 eq.) in 1 mL of CH_2Cl_2 while stirring at room temperature or -78 °C. An additional 0.5 mL of CH_2Cl_2 was used to transfer any residual oxidant into the reaction mixture. The resulting solutions were stirred for 1 hour before filtered through glass wool and solvent was removed *in vacuo*.

*10-(4-(dimesitylboraneyl)phenyl)phenothiazinyl hexafluoroantiminate (**3**$^{\bullet+}$)*

Synthesized following general procedure with **3** (50.0 mg, 0.95 mmol) and $NOSbF_6$ (25.4 mg, 0.95 mmol) at -78 °C, yielding a deep, red-coloured solid (0.072 g, 99 % yield). Crystals suitable for X-ray diffraction were obtained by vapour diffusion with pentanes and CH_2Cl_2 at -20 °C. ^{11}B, ^{13}C, and ^{19}F NMR spectra were not obtained due to the paramagnetic nature of **3**$^{\bullet+}$.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.96 (br, 4H), 2.43 (br, 6H), 2.28 (br, 12H). **ESI-MS** $C_{36}H_{34}BNS$ (m/z): $[M+H]^+$ calculated: 522.2536; found: 522.2528.

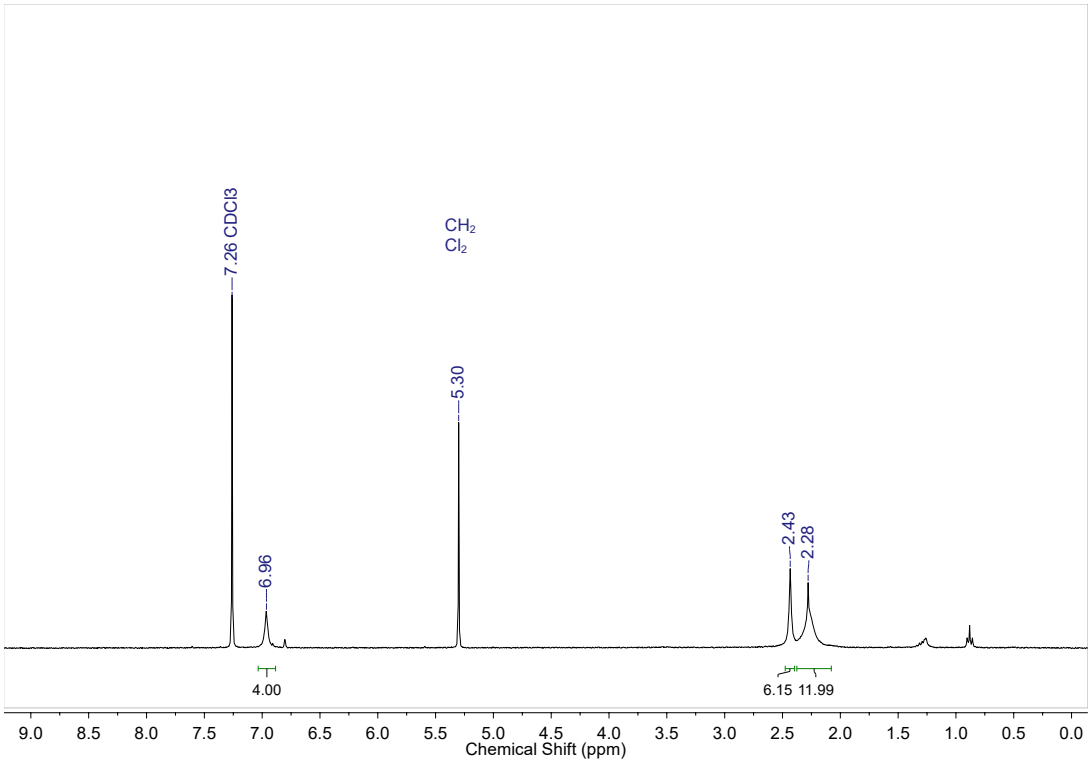


*Figure S1: ^{1}H NMR spectrum of **3**$^{\bullet+}$ in $CDCl_3$.*

S3 Cyclic Voltammetry of 1, 2, and 3

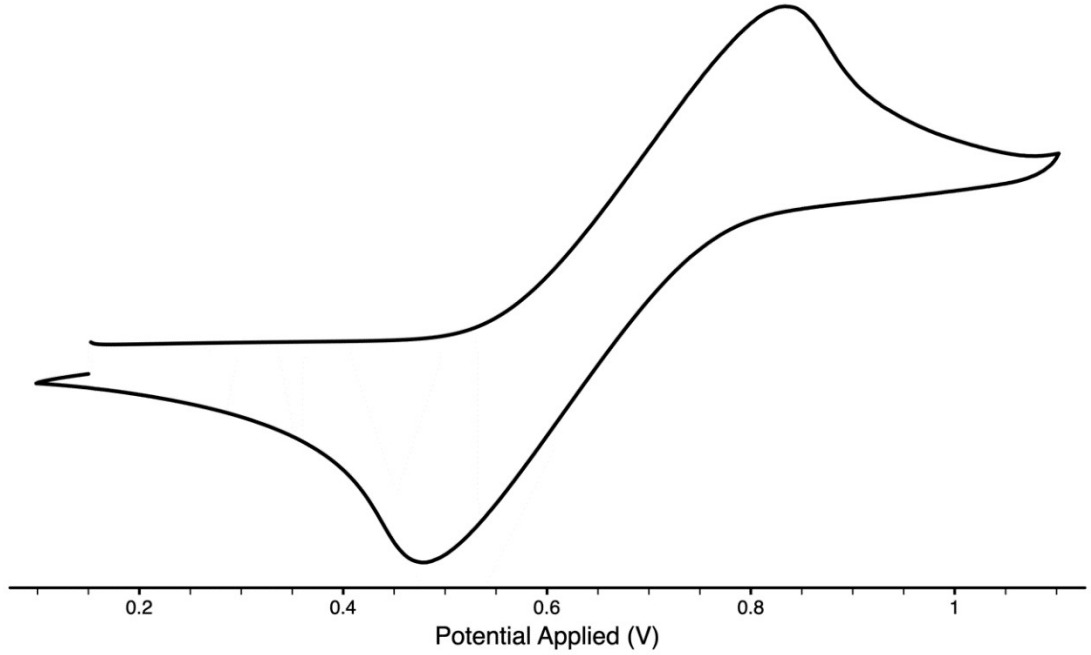


***Figure S2**: Cyclic voltammogram of **1** in CH_2Cl_2 (0.1 M $TBAPF_6$, 100 mV/s) zoomed in on reversible redox event.*

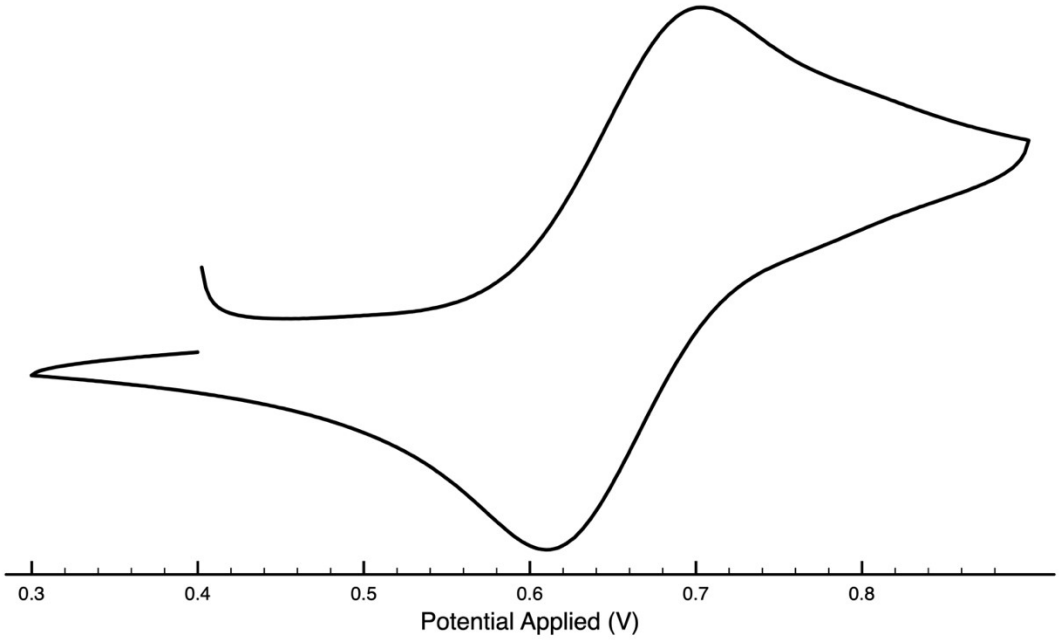


***Figure S3**: Cyclic voltammogram of **2** in CH_2Cl_2 (0.1 M $TBAPF_6$, 100 mV/s) zoomed in on reversible redox event.*

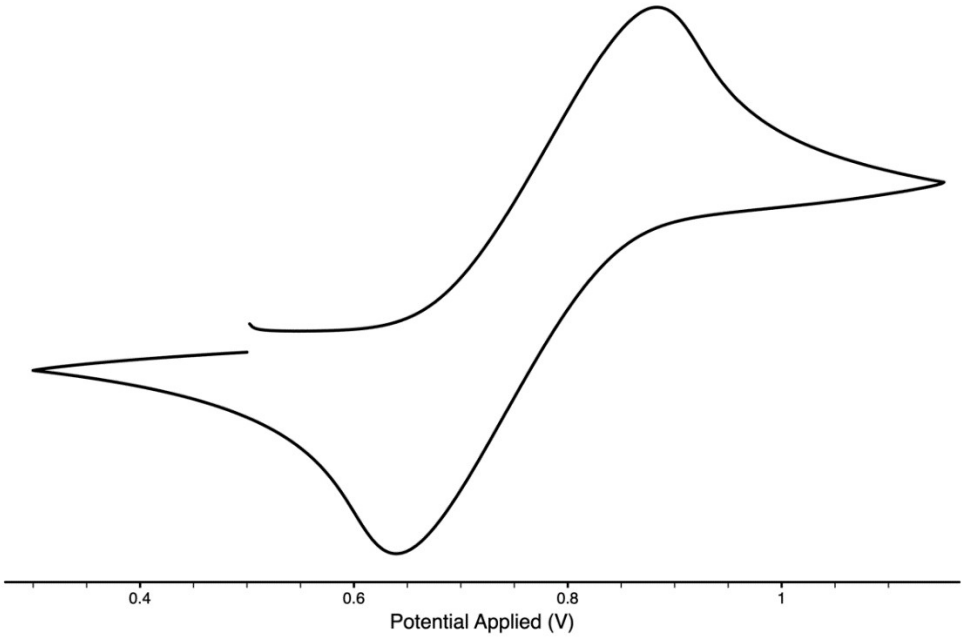


***Figure S4**: Cyclic voltammogram of **3** in CH_2Cl_2 (0.1 M $TBAPF_6$, 100 mV/s) zoomed in on reversible redox event.*

S4 Electron Paramagnetic Resonance (EPR) Spectroscopy of $1^{\bullet+}$, $2^{\bullet+}$, and $3^{\bullet+}$

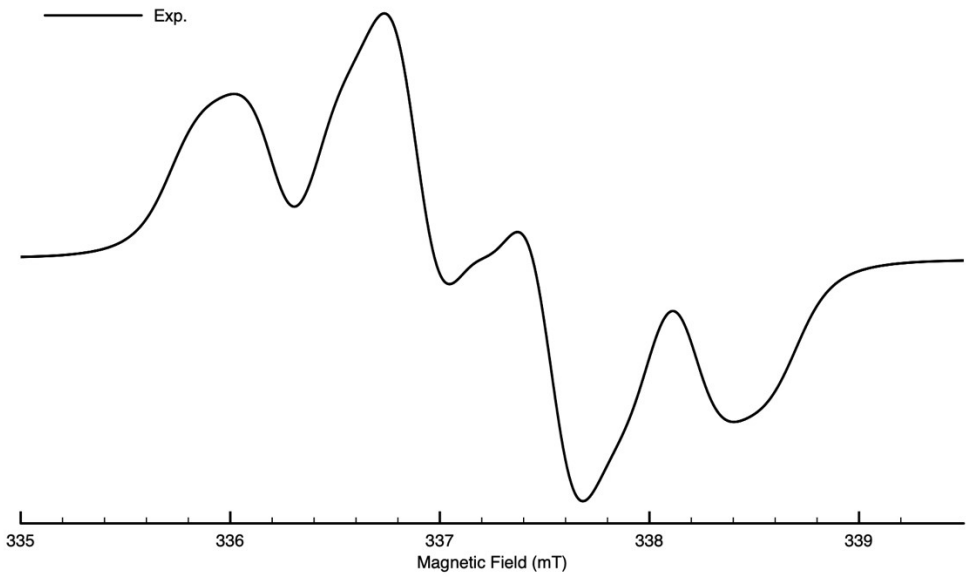


***Figure S5**: Experimental EPR spectrum of **1**$^{\bullet+}$ in CH_2Cl_2 at 298 K; frequency = 9.468 GHz, power = 10 mW, modulation = 1 mT.*

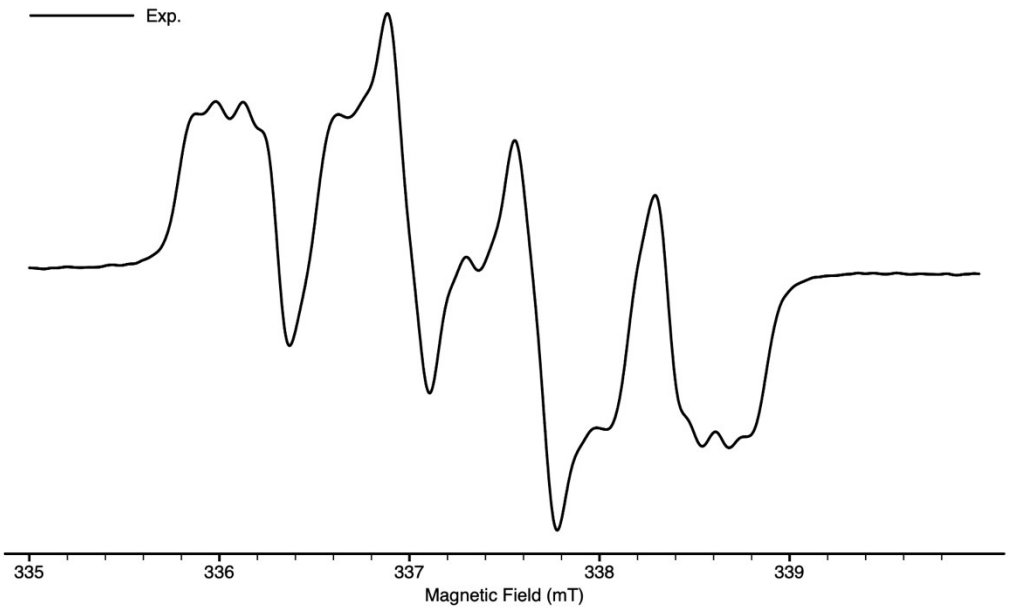


***Figure S6**: Experimental EPR spectrum of **2**$^{\bullet+}$ in CH_2Cl_2 at 298 K; frequency = 9.468 GHz, power = 10 mW, modulation = 1 mT.*

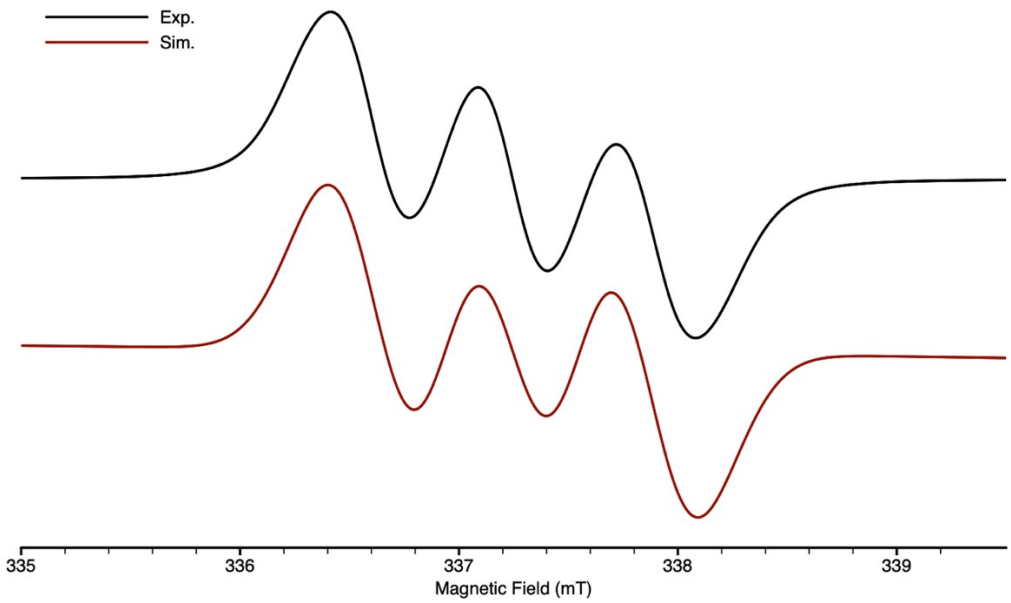


***Figure S7**: Experimental (black) and simulated (red) EPR spectra of **3**$^{\bullet+}$ in CH_2Cl_2 at 298 K; frequency = 9.468 GHz, power = 10 mW, modulation = 1 mT, simulation parameters: S = 1, g = 2.0058, A = 17.113, lw = 0.5569.*

S5 Lewis Acidity Assessment

S5.1 Gutmann-Beckett Analysis of 3, $3^{\bullet+}$ and $B(C_6F_5)_3$

General procedure for Gutmann-Beckett tests: Triethylphosphine oxide (TEPO) (0.0027 g, 0.020 mmol, 1 eq.) and **3, $3^{\bullet+}$ and $B(C_6F_5)_3$** (0.020 mmol, 1 eq.) were dissolved in CD_2Cl_2 in a J-Young NMR tube. The NMR tube was sealed and $^{31}P\{^1H\}$ NMR spectra were recorded. The acceptor number (AN) was calculated using the following formula: $AN = 2.21(\delta_{sample} - 41)$.[7,8]

Table S1: *Gutmann-Beckett analysis of compounds 1 and 2 using stoichiometric amounts of TEPO, including ^{31}P chemical shifts, full width at half maximum, and acceptor numbers*

Compound	^{31}P Chemical Shift (ppm)	Full Width at Half Maximum (FWHM, Hz)	Acceptor Number (AN)
3	50.5	2.0	0
$3^{\bullet+}$	64.4	2223.5	52
$B(C_6F_5)_3$	77.2	10.4	80

NMR spectra of Gutmann-Beckett tests with 3, $3^{\bullet+}$ and $B(C_6F_5)_3$

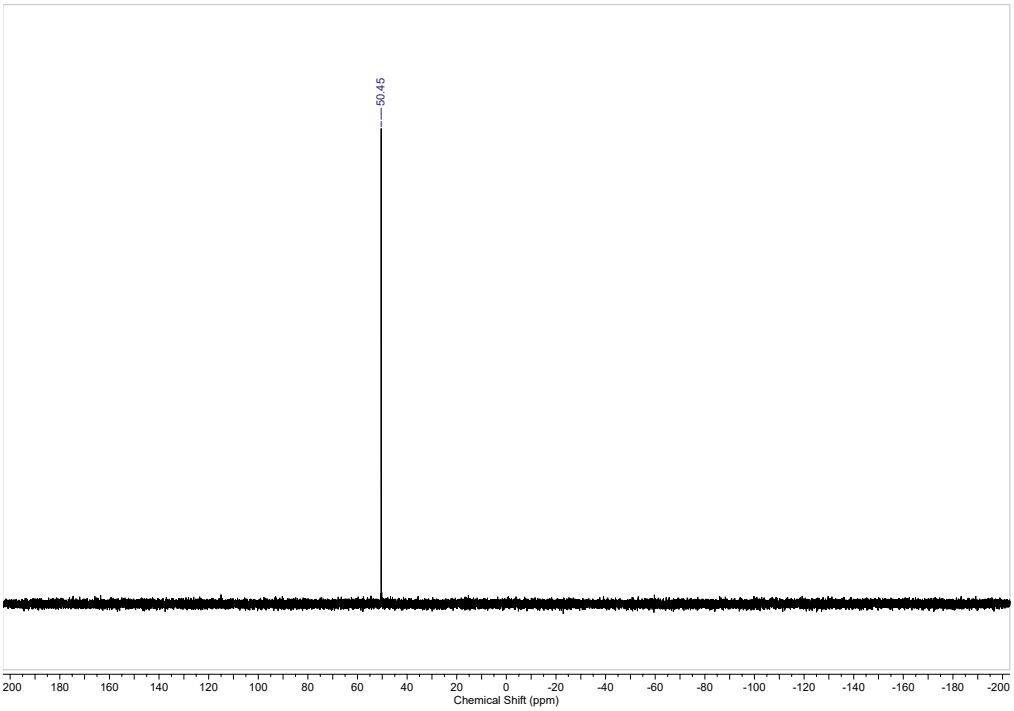


Figure S8: *$^{31}P\{^1H\}$ NMR spectrum of equimolar triethylphosphine oxide and **3**.*

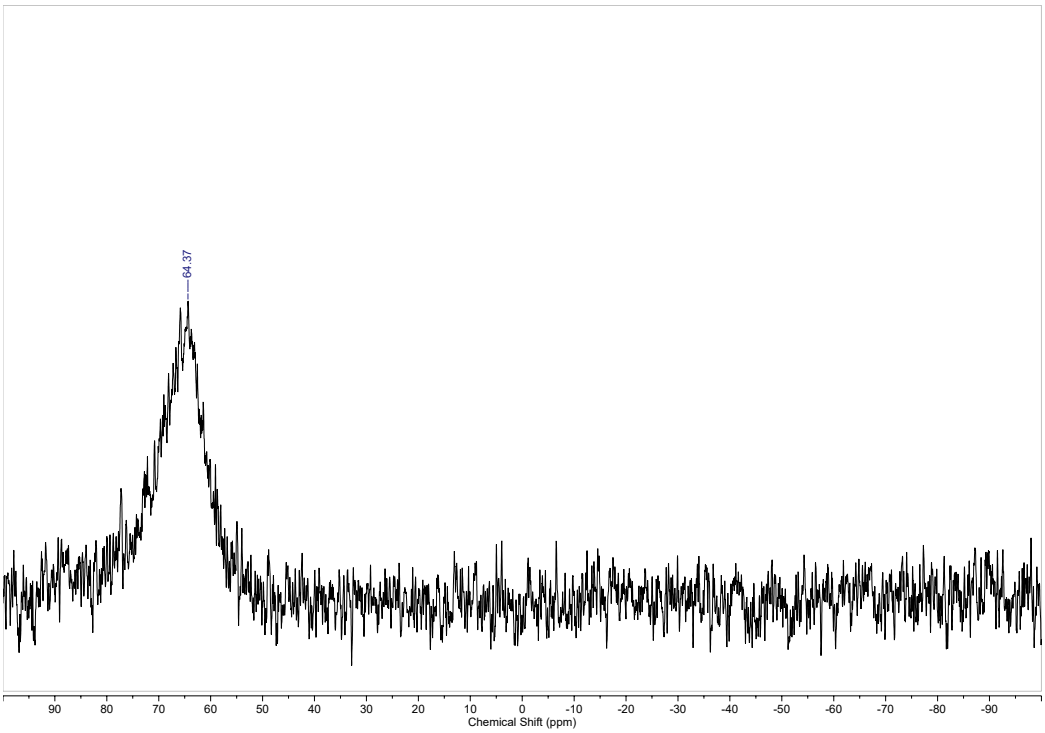


Figure S9: *$^{31}P\{^{1}H\}$ NMR spectrum of equimolar triethylphosphine oxide and* ***3^{++}****.*

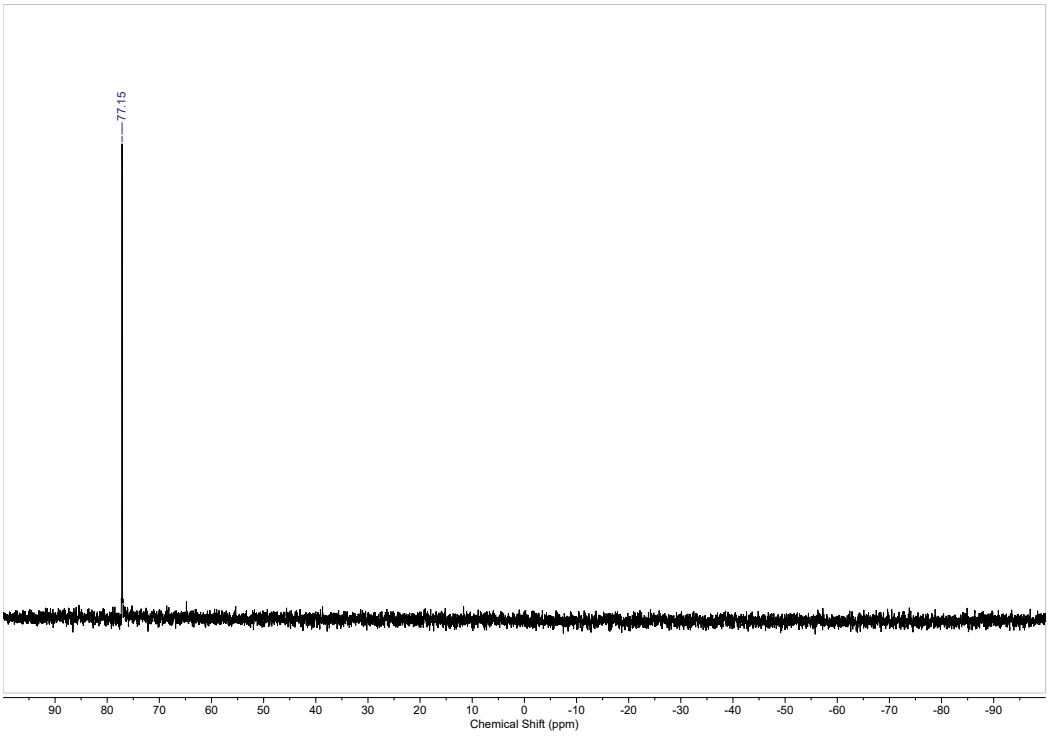


Figure S10: *$^{31}P\{^{1}H\}$ NMR spectrum of equimolar triethylphosphine oxide and* ***$B(C_6F_5)_3$****.*

S5.2 Computational Lewis Acidity Assessment

Fluoride ion affinity (FIA), hydride ion affinity (HIA), and ammonia affinity (AA) calculations were completed using Gaussian 16 suite of quantum chemistry programs.[9] The geometry optimizations of all molecules were carried out using B3LYP[10,11] level of theory and 6-31+G(d,p)[12–14] basis sets with conductor-like polarizable continuum (CPCM) dichloromethane solvation model.[15] The optimized structures were subjected to normal mode frequency calculations using the same computational methods. The results of the frequency analysis contained zero imaginary frequencies, showing that these structures converge to a stationary point on the potential energy surface. Thermochemical parameters, such as enthalpies, were obtained from the frequency calculations and used to determine the FIA, HIA and AA values following previously developed methods.[16–18]

Table S2: *Computational assessment of Lewis acidity[a]*

Compound	**FIA_{gas} (kJ/mol)**	**FIA_{solv}[b] (kJ/mol)**	**HIA_{gas} (kJ/mol)**	**HIA_{solv}[b] (kJ/mol)**	**AA_{gas} (kJ/mol)**	**AA_{solv}[b] (kJ/mol)**
SbF_5	496[16]	362[16]	535[19]	540[19]	163[19]	184[19]
$B(C_6F_5)_3$	444[16]	216[16]	484[19]	416[19]	122[19]	134[19]
3	243	165	473	234	22	25
$3^{\bullet+}$	507	213	763	285	33	33

[a] All calculations were performed using B3LYP/6-31+g(d,p) basis sets. [b] Solvated enthalpies were calculated with conductor-like polarizable continuum (CPCM)

S6 Stoichiometric Experiments

Addition of DMAP to $3^{\bullet+}$: a solution of 4-dimethylaminopyridine (DMAP, 1.6 mg, 0.132 mmol) in $CDCl_3$ was added to a solution of $\mathbf{3}^{\bullet+}$ (10 mg, 0.132 mmol) and transferred to an NMR tube in the glovebox. The NMR tube was sealed with Parafilm and ^{1}H NMR spectroscopy was performed on the mixture.

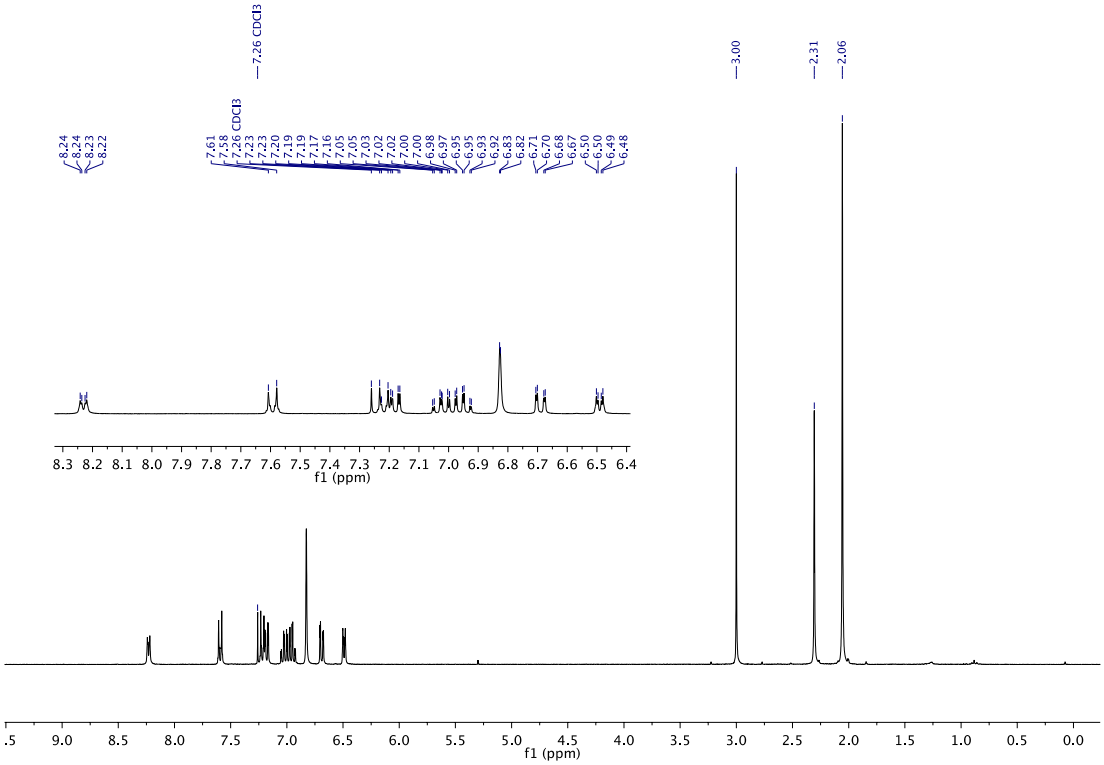


***Figure S11**: ^{1}H NMR spectrum of the control experiment of **3** and DMAP in $CDCl_3$.*

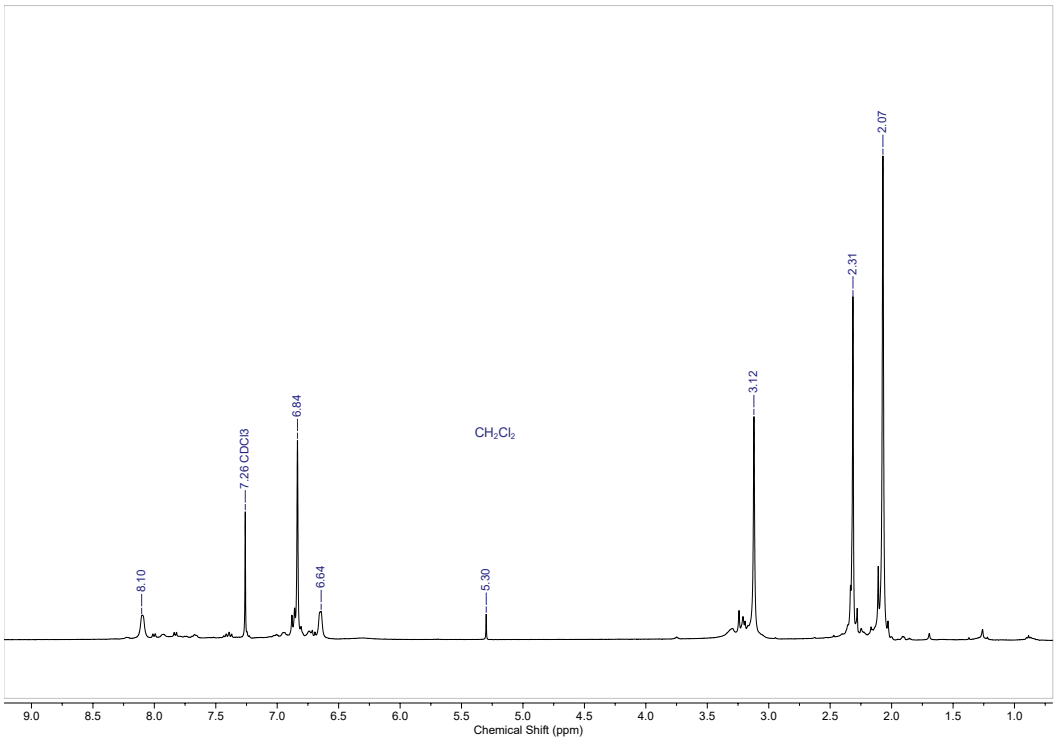


Figure S12: ^{1}H NMR spectrum of $3^{\bullet+}$ and DMAP in $CDCl_3$.

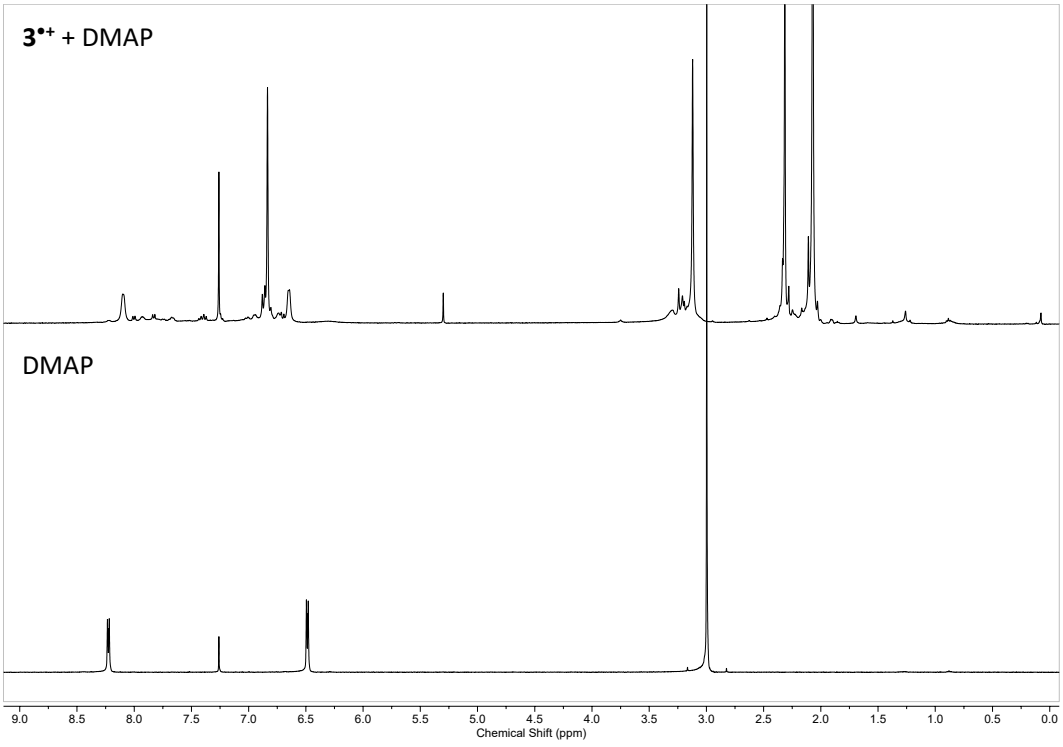


Figure S13: Stacked ^{1}H NMR spectra of $3^{\bullet+}$ and DMAP in $CDCl_3$.

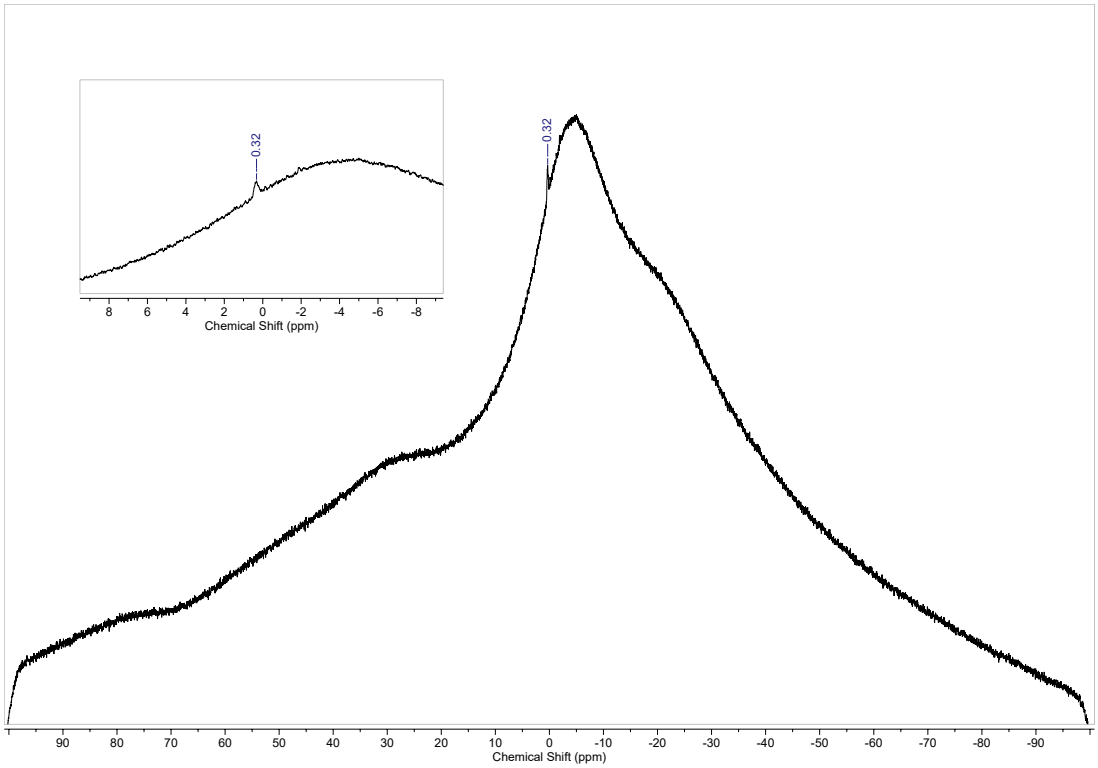


Figure S14: $^{11}B\{^{1}H\}$ NMR spectrum of $3^{\bullet+}$ and DMAP in $CDCl_3$.

Addition of $HSiEt_3$ to $3^{\bullet+}$: a solution of triethylsilane (1.6 mg, 0.132 mmol) in $CDCl_3$ was added to a solution of **$3^{\bullet+}$** (10 mg, 0.132 mmol) and transferred to an J Young tapped NMR tube in the glovebox. The NMR tube was sealed and ^1H and ^1H-^{29}Si heteronuclear multiple bond correlation (HMBC) NMR spectroscopy was performed on the mixture. NMR chemical shifts of $FSiEt_3$ is consistent with literature reports.

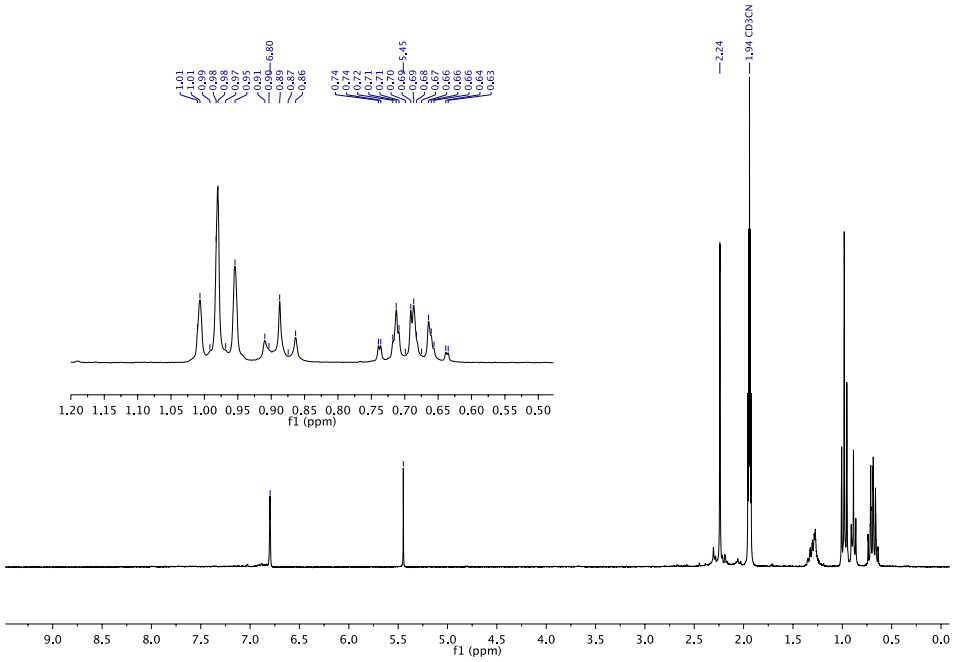


Figure S15: ^1H NMR spectrum of $3^{\bullet+}$ and $HSiEt_3$ in CD_3CN.

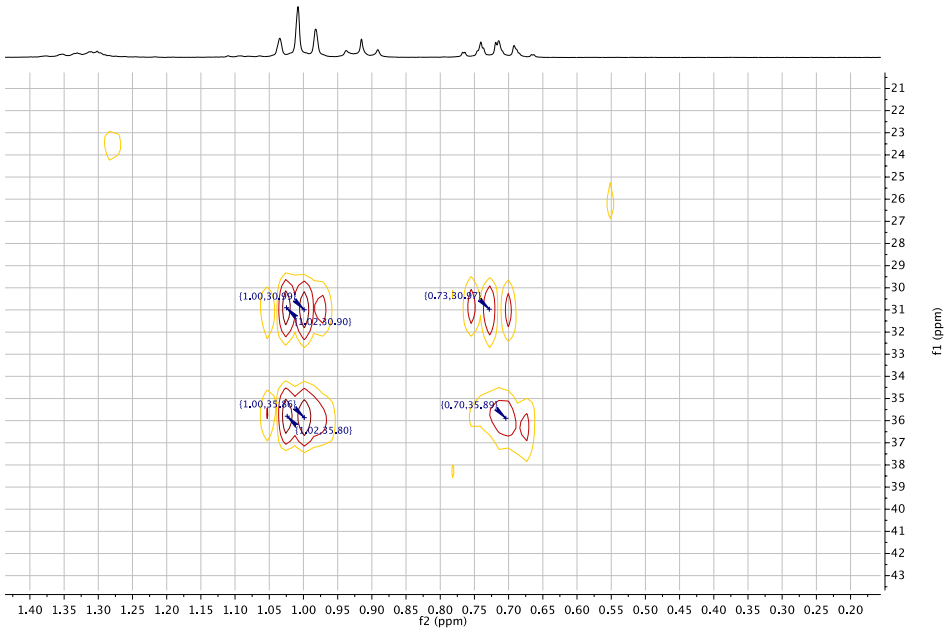


***Figure S16**: ^1H-^{29}Si HMBC NMR spectrum of **$3^{\bullet+}$** and $HSiEt_3$ in CD_3CN.*

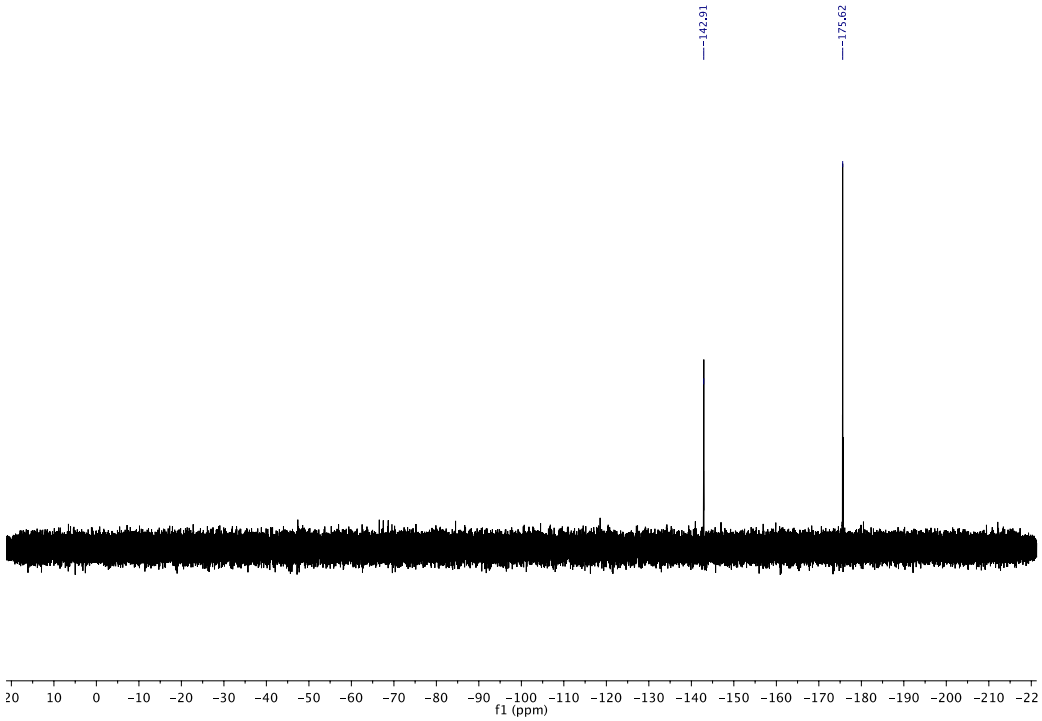


Figure S17: $^{19}F\{^{1}H\}$ NMR spectrum of $3^{\bullet+}$ and $HSiEt_3$ in CD_3CN.

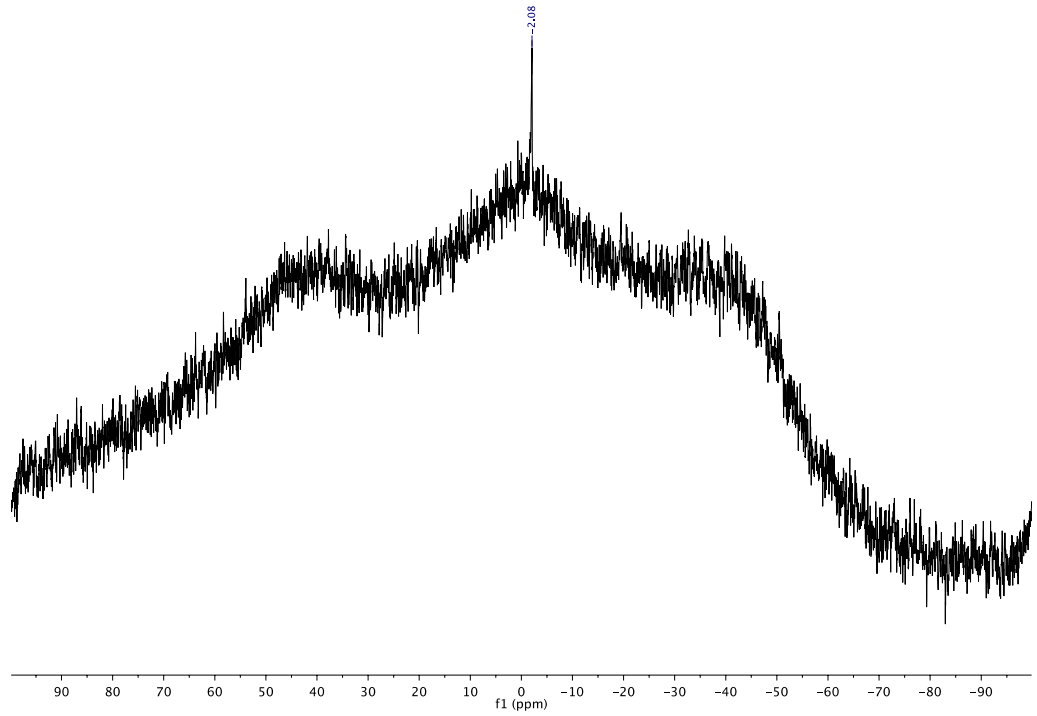


Figure S18: $^{11}B\{^{1}H\}$ NMR spectrum of $3^{\bullet+}$ and $HSiEt_3$ in CD_3CN.

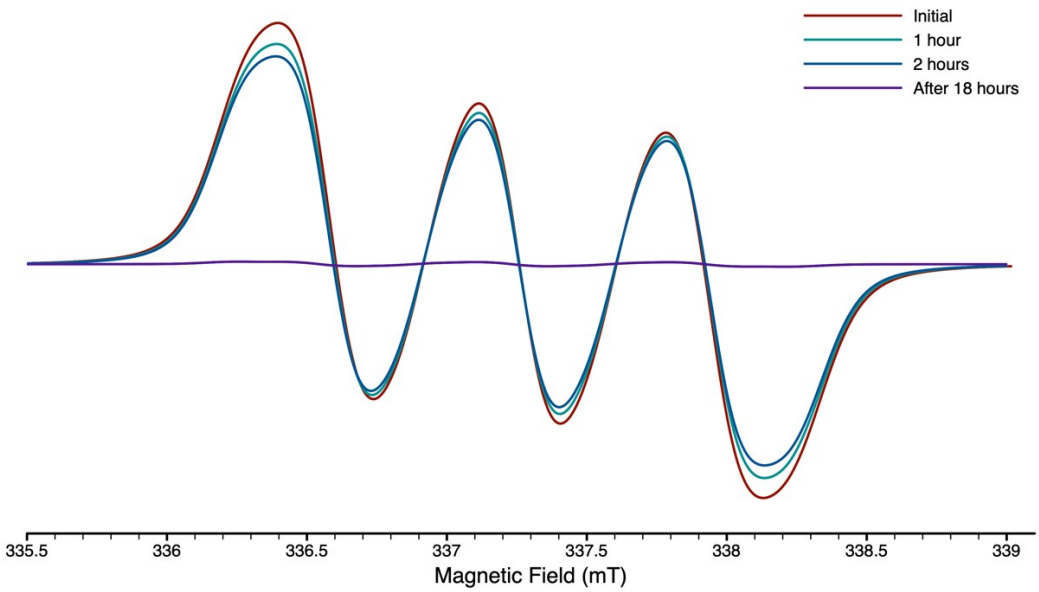


***Figure S19**: Overlayed experimental EPR spectra of **3**$^{\bullet+}$ and $HSiEt_3$ in CD_3CN after 1 hour, 2 hours, and 18 hours; frequency = 9.468 GHz, power = 10 mW, modulation = 1 mT.*

Addition of 9,10-dihydroanthracene: a solution containing the 9,10-dihydroanthracene (0.5 mg, 0.028 mmol mmol, 1eq.) was added to a solution of **3**$^{\bullet+}$ (4.2 mg, 0.056 mmol, 2 eq.) in 0.6 mL of CD_3CN. The mixture was dispensed into sealed NMR tubes, sealed with Parafilm, and allowed to react over time at room temperature for 2 days and then heated to 40 °C while monitoring *via* ^{1}H NMR spectroscopy. A control experiment heating 9,10-dihydroanthracene without catalyst was performed in parallel. The reaction was complete upon consumption of starting material or no observable progression in conversion. Chemical shifts of the silyl ether products were consistent with the literature.

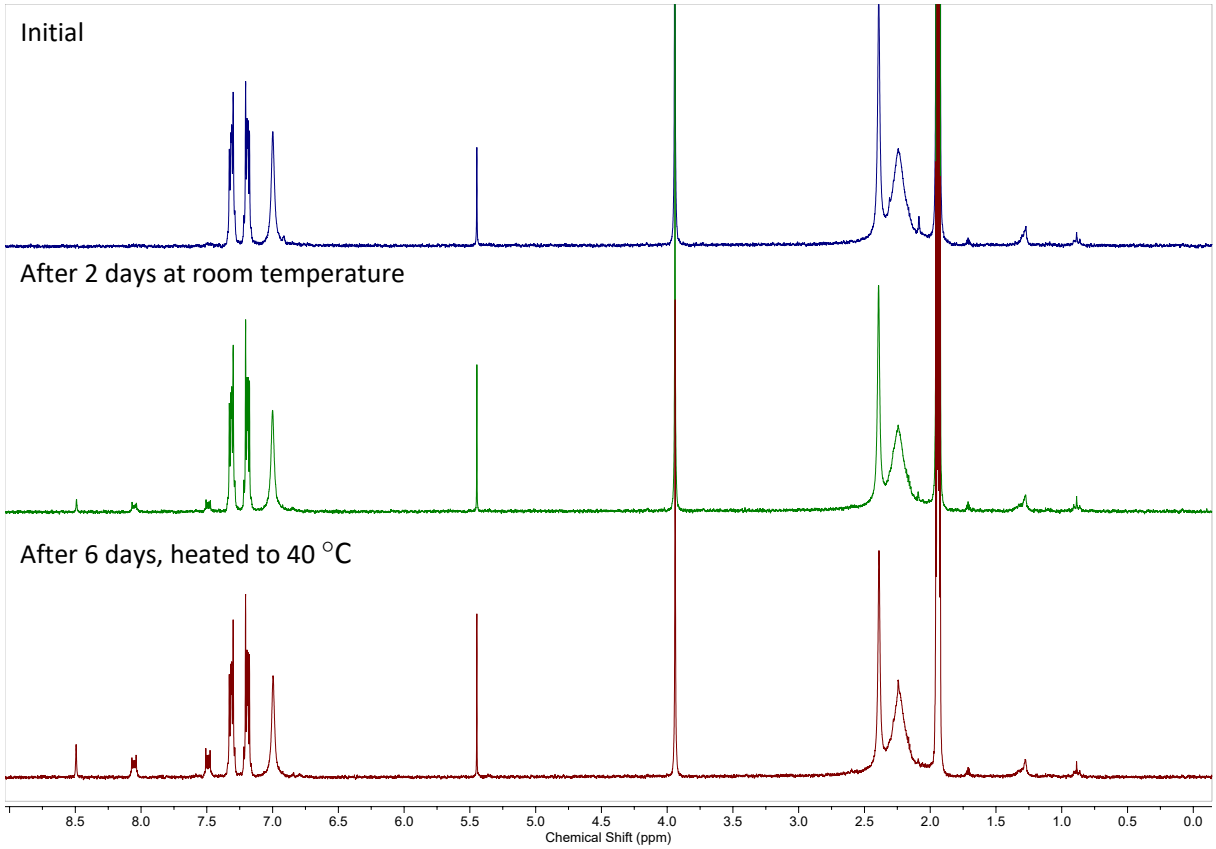
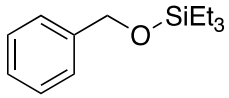


***Figure S20**: ^{1}H NMR spectrum of **3**$^{\bullet+}$ and 9,10-dihydroanthracene in CD_3CN.*

S7 Catalytic Experiments

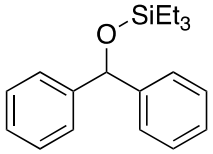
General procedure for hydrosilylation experiments: a mixture containing the corresponding carbonyl substrate (0.100 mmol, 1eq.), triethylsilane (0.110 mmol, 1.1 eq.), and **3**$^{\bullet+}$ (3.6 mg, 0.005 mmol, 5 mol %) in 0.6 mL deuterated solvent ($CDCl_3$ or CD_3CN) was prepared. The mixture was dispensed into sealed NMR tubes, sealed with Parafilm, and allowed to react over time while monitoring *via* quantitative ^{1}H NMR spectroscopy. Control experiments for the hydrosilylation reactions without catalyst were performed in parallel. The reaction was complete upon consumption of starting material or no observable progression in conversion. Chemical shifts of the silyl ether products were consistent with the literature.

((Triethylsiloxy)methyl)benzene:



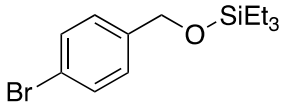
^{1}H NMR (600 MHz, CD_3CN) δ: 7.38-7.27 (m, 5H), 4.55 (s, 2H), 0.95 (t, 9H, *J* = 7.9 Hz), 0.54 (q, 6H, *J* = 7.9 Hz).

1,1'-(((Triethylsilyl)oxy)methylene)bisbenzene:



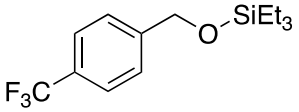
^{1}H NMR (300 MHz, CD_3CN) δ: 7.36 – 7.12 (m, 10H), 3.99 (s, 1H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.57 (q, *J* = 7.8 Hz, 6H).

4-Bromo((triethylsiloxy)methyl)benzene:



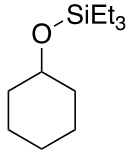
^{1}H NMR (300 MHz, CD_3CN) δ: 7.54 (d, *J* = 8.3 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 2H), 4.54 (s, 2H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.57 (q, *J* = 7.9 Hz, 6H).

4-Trifluoromethyl((triethylsiloxy)methyl)benzene:



^{1}H NMR (300 MHz, CD_3CN) δ: 7.71 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 4.70 (s, 2H), 0.97 (t, *J* = 7.9 Hz, 8H), 0.57 (q, *J* = 7.9 Hz, 6H).

((Triethylsilyl)oxy)cyclohexane:



^{1}H NMR (600 MHz, CD_3CN) δ: 3.34 (s, 1H), 1.81 (m, 2H), 1.69 (m, 2H), 1.51 (m, 1H), 1.30-1.14 (m, 4H), 0.94 (t, *J* = 8.0 Hz, 9H), 0.54 (q, *J* = 8.0 Hz, 6H).

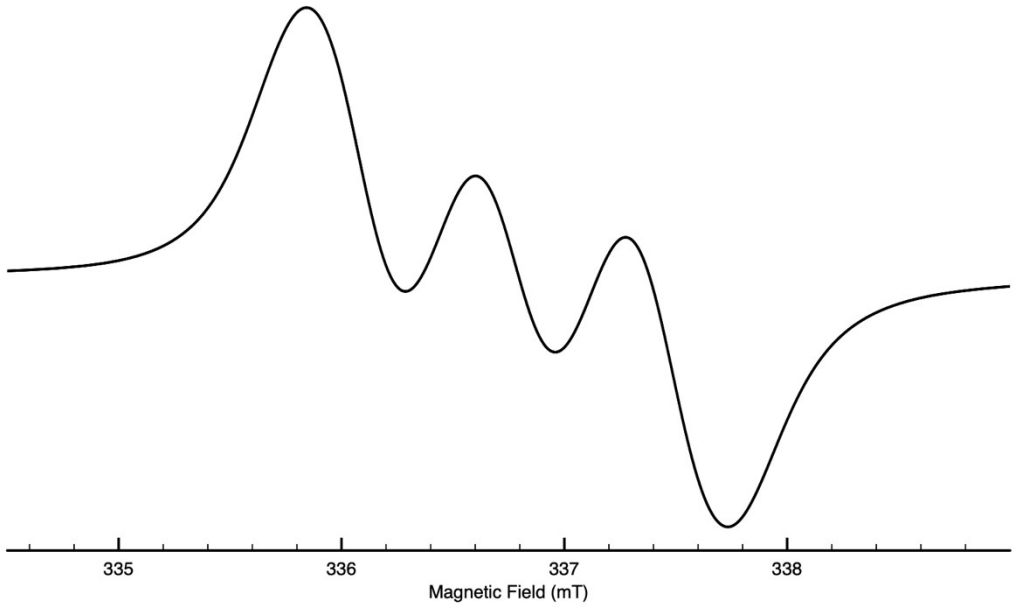
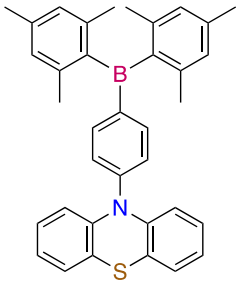


***Figure S21**: Experimental EPR spectra of **3**$^{\bullet+}$ in CH_2Cl_2 at 298 K after completion of the hydrosilylation of 4-bromobenzaldehyde, frequency = 9.468 GHz, power = 10 mW, modulation = 1 mT.*

S8 Computational Details

S8.1 Optimized Coordinates for Lewis Acidity Assessment

(10-Phenylphenothiazinyl)dimesitylborane (**3**)



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C	-2.98969600	2.53964200	-0.16525500
C	-3.68149500	3.68060900	0.26174500
C	-4.60505700	3.63948500	1.30872300
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H	-3.49373800	4.62709400	-0.24200600
B	-2.47345600	-0.02300000	-0.02705400
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C	-2.96251900	-2.59091900	0.10989400
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H	-3.44334500	-4.68369900	0.18423400
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H	-4.93865100	-0.81257100	1.53391600
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H	-3.67375700	0.43812200	-2.76152100
H	-5.29405100	-0.19615000	-3.04135500
C	-5.25598400	-4.96314200	-1.84144100

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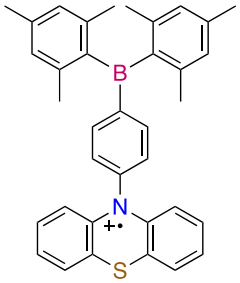
H	5.97192600	3.75779000	-2.75233800
H	5.97116400	-2.99504100	3.56223200
S	6.25144200	-0.70914000	-0.76062300
N	3.37897000	-0.03760500	-0.04377700

(10-Phenylphenothiazinyl)dimesitylborane radical cation (**3**$^{\bullet+}$)



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C	-2.88299700	-2.56188000	0.02914200
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C	-3.58124100	-3.68890800	-0.41866600
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C	-4.56336300	-3.60254700	-1.40987900
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H	-5.62422600	-2.24738600	-2.69842700
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C	3.24685900	1.96501300	-1.41896500
C	5.43435100	1.10142200	-0.79941100
C	5.43416800	-1.10165800	0.79949500

C	3.24650900	-1.96498000	1.41884100
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H	2.16816100	-1.91394900	1.37832100
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C	5.26000700	3.05709600	-2.21606000
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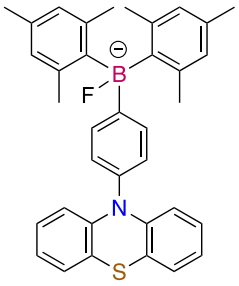
H	5.73150100	-3.84686900	2.78950900
S	6.51688300	-0.00017700	0.00008700
N	3.38153800	-0.00001200	-0.00004000

Fluoride adduct of (10-Phenylphenothiazinyl)dimesitylborane (**3-F**)



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C	-4.32006200	-1.87093400	0.23276100
C	-2.21924400	-2.42775400	-0.81614100
C	-4.90440000	-2.99871800	-0.36033300
C	-2.83700600	-3.54915600	-1.40040800
C	-4.17810800	-3.86286500	-1.18340900
C	-0.74139300	0.06050700	0.74669600
C	0.16658500	-0.56938300	1.61438400
C	-0.16349800	0.95615500	-0.16702300
C	1.54764300	-0.36286700	1.56057200
H	-0.21705400	-1.26369700	2.35757800
C	1.21336700	1.18058600	-0.25354100
H	-0.80645900	1.50236200	-0.85274600
C	2.09629500	0.51513300	0.61165200
H	2.19307300	-0.89404600	2.25028500

H	1.59362600	1.87202500	-0.99620200
C	4.03640500	1.30088300	-0.66298200
C	4.36866700	-0.22258400	1.15766100
C	4.05567000	2.68327200	-0.86386300
C	4.53507400	0.45058700	-1.66211600
C	4.90899900	-1.26251300	0.38541400
C	4.67205600	-0.14776800	2.51929100
C	4.51523300	3.21254000	-2.07127200
H	3.68456900	3.32870500	-0.07451400
C	5.01543300	0.97851600	-2.86566200
C	5.71753300	-2.23811400	0.97909400
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C	4.98699000	2.35873500	-3.07431000
H	4.50998800	4.28652000	-2.22672000
H	5.41157100	0.31443400	-3.62738200
C	5.97663500	-2.17951800	2.34976400
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H	5.67770400	-1.07558800	4.18125400
H	5.35236600	2.76677300	-4.01136300
H	6.59712600	-2.94135800	2.81089000
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C	-2.76090000	2.05298200	2.87419200
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H	-4.56775100	2.90954600	-2.11681000
H	-5.14853200	5.20753400	-1.46795400
H	-4.81350500	5.78491000	0.17506500
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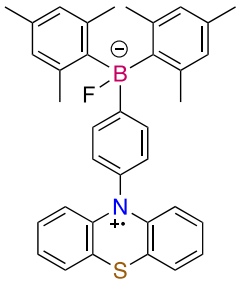
H	-3.53723500	1.11376500	-2.94807700
H	-2.38431100	0.13156000	-2.03269100
H	-4.08755900	-0.27361300	-1.99437100
H	-5.52310700	-0.08976600	0.48092000
H	-6.17282800	-1.52517700	1.28779800
H	-5.84436100	-4.90049000	-2.09976000
H	-4.84271600	-5.92220200	-1.06841900
H	-4.25184100	-5.44128700	-2.66206000
H	-4.78130700	-0.64885900	1.96957800
H	-0.59188700	-1.23524800	-1.63885000
H	-0.09576100	-2.28094400	-0.33310900

H	-0.45375700	-2.97702900	-1.92146500

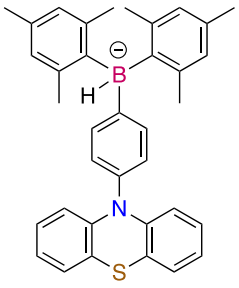
Fluoride adduct of (10-Phenylphenothiazinyl)dimesitylborane radical cation (**3$^{\bullet+}$-F**)



C	5.46534600	-2.35342500	0.75177200
C	4.66307800	-1.21089700	0.87112300
C	3.27497300	-1.24028300	0.54619200
C	2.76681800	-2.48304500	0.08744200
C	3.60086500	-3.61073800	-0.02497600
C	4.95447400	-3.57519700	0.30612700
H	6.52171800	-2.28387600	1.00797400
H	3.17301000	-4.54484100	-0.38554800
B	2.42036700	0.15656900	0.79067300
C	2.97357400	1.45372900	-0.06963100
C	2.86981800	2.77029500	0.45687800
C	3.48007100	1.34247900	-1.39093700
C	3.32446500	3.88025600	-0.27093800
C	3.92009300	2.47444500	-2.09747600
C	3.87432600	3.75674300	-1.54932800
H	3.23171200	4.87188100	0.17023600
H	4.30367400	2.34618700	-3.10866300
C	5.36776800	0.05987000	1.30824000
H	5.50026000	0.74204000	0.46116100
H	4.79574800	0.60178600	2.06159800
H	6.35927900	-0.17183400	1.71070000
C	1.32880800	-2.69561400	-0.35058700
H	1.04007700	-2.01769500	-1.15867700
H	1.19356700	-3.72011800	-0.71089800
H	0.61701400	-2.52840200	0.46114400
C	5.82596600	-4.80552800	0.21295700
H	6.82123600	-4.56256800	-0.17476500
H	5.96855900	-5.26864200	1.19782500
H	5.37984300	-5.56012100	-0.44240600
C	2.24019800	3.06131300	1.80593900
H	2.87252300	2.72422700	2.63158200
H	2.06735100	4.13689800	1.91806100
H	1.28480500	2.54219000	1.92215800
C	3.57386100	0.02075700	-2.13127400
H	4.40402500	-0.59235200	-1.76762200
H	2.67172200	-0.58386800	-2.01701400
H	3.72815100	0.19906100	-3.20046200
C	4.39616600	4.95798800	-2.30222500

H	4.36877900	4.79310300	-3.38412700
H	3.81032000	5.85581700	-2.07846000
H	5.43757100	5.17607500	-2.03211000
C	0.79812600	0.10019400	0.56623200
C	0.17835800	0.44756300	-0.64849800
C	-0.05493500	-0.26076400	1.62640900
C	-1.20403500	0.38839200	-0.82637600
H	0.79198400	0.77075800	-1.48376600
C	-1.44166000	-0.32343300	1.48295400
H	0.38426600	-0.50868400	2.58751500
C	-1.99973900	-0.00853500	0.24604800
H	-1.66367700	0.64442000	-1.77638900
H	-2.08381500	-0.61728600	2.30811600
C	-3.95714200	-1.32204100	-0.33961300
C	-4.19015700	1.04582200	0.32721000
C	-3.07796100	-2.40684700	-0.57701100
C	-5.34828600	-1.53531100	-0.53347000
C	-5.60423500	1.07608000	0.19332500
C	-3.53454500	2.23176600	0.73819700
C	-3.56441100	-3.63489800	-0.98171600
H	-2.01573500	-2.26682200	-0.43913800
C	-5.82515100	-2.79299300	-0.94470000
C	-6.31902900	2.25734300	0.46128000
H	-2.45978200	2.22994900	0.84841400
C	-4.25316800	3.38290000	0.99721900
C	-4.94479100	-3.83691700	-1.16742800
H	-2.86811500	-4.44746200	-1.15649100
H	-6.89183500	-2.93332500	-1.08574900
C	-5.65364500	3.40339100	0.85917800
H	-7.39853900	2.25807700	0.35229900
H	-3.72516800	4.27678700	1.31003700
H	-5.32027900	-4.80324200	-1.48450400
H	-6.21200800	4.30990600	1.06353500
S	-6.55140400	-0.30097900	-0.29224300
N	-3.43995400	-0.09707800	0.07082800
F	2.58738800	0.39502000	2.25221400

Hydride adduct of (10-Phenylphenothiazinyl)dimesitylborane (**3-H**)



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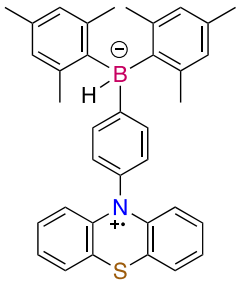
C	-3.22062900	1.16864300	0.50468400

C	-3.69674000	1.51144600	-0.78669800
C	-4.36059900	2.72831500	-1.02192500
C	-4.57654100	3.66385600	-0.00838900
B	-2.42684700	-0.22754400	0.86204600
C	-3.00770200	-1.56349000	0.08913800
C	-4.34260700	-1.96165100	0.39721300
C	-2.31520400	-2.39313700	-0.83426700
C	-4.92402700	-3.10319700	-0.17255900
C	-2.92328600	-3.53526600	-1.38613800
C	-4.22760000	-3.91741000	-1.06988200
C	-0.81846300	0.03613200	0.80058400
C	0.07658700	-0.71036400	1.58849800
C	-0.21080400	1.01578600	-0.00286200
C	1.46281500	-0.53706900	1.55890600
H	-0.32474800	-1.47856600	2.24832100
C	1.17257000	1.21711300	-0.05951300
H	-0.83952900	1.64544200	-0.62888900
C	2.03627600	0.43431800	0.72186800
H	2.09189400	-1.16082700	2.18323600
H	1.57263300	1.97933400	-0.71810300
C	3.99532900	1.38294100	-0.40672500
C	4.29296700	-0.44129400	1.12007500
C	4.03429100	2.77912300	-0.36642700
C	4.48403900	0.71140900	-1.53805300
C	4.81537500	-1.34135200	0.17805600
C	4.59567700	-0.61171200	2.47349400
C	4.50616700	3.50236200	-1.46319000
H	3.66783400	3.28352100	0.52166000
C	4.97810400	1.43233600	-2.63098300
C	5.60177700	-2.42229900	0.59179100
H	4.20342400	0.10453800	3.18795600
C	5.36246100	-1.70067900	2.89230800
C	4.97088500	2.82801200	-2.59779700
H	4.51636300	4.58703900	-1.43074200
H	5.36702800	0.90407100	-3.49578800
C	5.85764500	-2.61002800	1.95140800
H	6.01238600	-3.10524700	-0.14521400
H	5.57723400	-1.83576900	3.94744200
H	5.34631400	3.38645600	-3.44941700
H	6.46072100	-3.45359900	2.27195400
S	4.47538500	-1.07337900	-1.55348600
N	3.45842200	0.63855600	0.69017500
C	-0.90876000	-2.09796900	-1.32104400
C	-5.20618700	-1.15445300	1.34329600
C	-4.85069700	-5.16602500	-1.65004700
C	-3.50317200	0.59898300	-1.98073200
C	-2.89180600	1.93105400	2.92599100
C	-5.32511500	4.95126300	-0.26640500
H	-5.94957000	-3.36109900	0.09072800
H	-2.35802600	-4.13772200	-2.09661100
H	-4.20204200	4.07351000	2.06882300

H	-4.70848000	2.95256100	-2.02993000
H	-5.29909400	5.22081000	-1.32728800
H	-4.90099600	5.78338700	0.30626200
H	-6.38105800	4.86697900	0.02263600
H	-3.01787700	2.83667300	3.52925000
H	-3.41475500	1.10810200	3.42587800
H	-1.83132100	1.66069400	2.92031300
H	-3.73264400	1.12965000	-2.91112100
H	-2.47594900	0.23227800	-2.04184900
H	-4.14391800	-0.28659700	-1.92561200
H	-5.40054700	-0.15182400	0.94920200
H	-6.16695600	-1.65115300	1.51479300
H	-5.91531500	-5.02063000	-1.86414000
H	-4.77513000	-6.01339600	-0.95574500
H	-4.35488900	-5.46266700	-2.58013900
H	-4.70763800	-1.00544700	2.30676700
H	-0.80501400	-1.07009100	-1.67657000
H	-0.16223700	-2.21708900	-0.53097800
H	-0.64406600	-2.77151200	-2.14313400
H	-2.65000900	-0.48159700	2.04447500

Hydride adduct of (10-Phenylphenothiazinyl)dimesitylborane radical cation (**3•⁺-H**)



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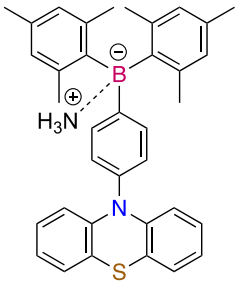
C	-4.60405800	-1.23522800	-1.20429700
C	-3.27245700	-1.20558300	-0.69375900
C	-2.77938400	-2.43444800	-0.17925500
C	-3.56968300	-3.59809000	-0.19246700
C	-4.86895900	-3.61552400	-0.70007900
H	-6.38459100	-2.37937000	-1.59256800
H	-3.15591800	-4.51696600	0.22125600
B	-2.47571800	0.23167500	-0.79046500
C	-3.11275500	1.44821500	0.11254100
C	-3.07908300	2.77954900	-0.38680400
C	-3.66229900	1.28104700	1.40928000
C	-3.60644400	3.85088900	0.34878500
C	-4.18398300	2.37160100	2.12646900
C	-4.18052200	3.66889800	1.61080700
H	-3.56182100	4.85485500	-0.07194300
H	-4.59590200	2.19999100	3.12028700
C	-5.26200400	0.00987900	-1.75979900
H	-5.34649400	0.79099200	-0.99776500

H	-4.66888500	0.44514400	-2.57116800
H	-6.26425000	-0.21465100	-2.13861800
C	-1.40582500	-2.58298100	0.44931300
H	-1.19931000	-1.79798900	1.18006900
H	-1.32529000	-3.54876100	0.95871900
H	-0.60316500	-2.52903500	-0.29248500
C	-5.69208900	-4.88231600	-0.72950400
H	-6.74030600	-4.68529200	-0.47914500
H	-5.68103300	-5.34496400	-1.72504800
H	-5.30721300	-5.62285200	-0.02108200
C	-2.45926600	3.10254400	-1.73056900
H	-3.02199300	2.64780300	-2.55311800
H	-2.42701800	4.18522400	-1.89197000
H	-1.43923500	2.71203800	-1.80497300
C	-3.70338200	-0.06842900	2.09676000
H	-4.43457000	-0.73909400	1.63542400
H	-2.73872300	-0.57837700	2.03984000
H	-3.96501000	0.04699100	3.15384400
C	-4.78052500	4.82543100	2.37626500
H	-4.81028500	4.61891600	3.45096400
H	-4.20933700	5.74729800	2.22216000
H	-5.81058300	5.02697000	2.05435200
C	-0.86027200	0.18867200	-0.58016500
C	-0.21437200	0.67353800	0.57442000
C	-0.01977800	-0.32073800	-1.59195800
C	1.16967100	0.60952500	0.74544100
H	-0.81643400	1.10138000	1.37124300
C	1.36550700	-0.39907800	-1.45449600
H	-0.47232000	-0.68271200	-2.51216700
C	1.94551200	0.06004400	-0.27240200
H	1.64478900	0.97017900	1.65333800
H	1.99168200	-0.81119900	-2.24060300
C	3.87080000	-1.22348700	0.46510400
C	4.16469100	1.03249500	-0.49751600
C	2.96413500	-2.24648700	0.83661700
C	5.25642100	-1.44787800	0.68444300
C	5.57977700	1.04024100	-0.37135700
C	3.53980000	2.17405100	-1.05582100
C	3.41931500	-3.42659700	1.39224400
H	1.90562900	-2.09661800	0.68126800
C	5.70110000	-2.65590900	1.25096500
C	6.32525300	2.15712500	-0.78920700
H	2.46468400	2.18709100	-1.16225200
C	4.28839800	3.26201100	-1.46159500
C	4.79435900	-3.63993900	1.60304000
H	2.70241800	-4.19235500	1.66674900
H	6.76408700	-2.80543100	1.40879400
C	5.68964100	3.26095100	-1.32972300
H	7.40486700	2.14149400	-0.68255500
H	3.78365900	4.12295700	-1.88551200
H	5.14535000	-4.56829600	2.03927000

H	6.27166700	4.11797200	-1.64921300
S	6.49151600	-0.28777100	0.28703200
N	3.38430200	-0.04643700	-0.09583500
H	-2.60335300	0.53996500	-1.97101300

Ammonia adduct of (10-Phenylphenothiazinyl)dimesitylborane (**3-NH$_3$**)



C	-5.28562600	2.49661900	1.03743300
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C	-3.23064400	1.21956100	0.55835000
C	-2.68063000	2.43357800	0.05732300
C	-3.41952400	3.62614400	0.09416500
C	-4.71897600	3.69198500	0.59871900
H	-6.31582800	2.49586600	1.38922700
H	-2.96564900	4.53204100	-0.30282100
B	-2.42150700	-0.21669600	0.65661700
C	-3.03905000	-1.46409700	-0.21797500
C	-2.83163100	-2.81817600	0.16710000
C	-3.73540800	-1.26200000	-1.44237600
C	-3.39440300	-3.87691700	-0.56156800
C	-4.27853500	-2.34462300	-2.15012400
C	-4.15079400	-3.66404800	-1.71368900
H	-3.21526500	-4.89721200	-0.22748700
H	-4.80731700	-2.14725000	-3.08063100
C	-5.37109600	0.07223200	1.47816800
H	-5.03798700	-0.85083700	1.00146700
H	-5.33305500	-0.06075100	2.56786500
H	-6.42796200	0.20348000	1.22882100
C	-1.32032700	2.54325600	-0.60732200
H	-1.14266900	1.73901400	-1.32337500
H	-1.24784800	3.49327000	-1.14447900
H	-0.49841700	2.50415300	0.11168800
C	-5.47523800	4.99676300	0.66225500
H	-6.55577800	4.83466500	0.59944700
H	-5.27793300	5.52110000	1.60590800
H	-5.18056200	5.66850400	-0.15008900
C	-1.95804400	-3.23002600	1.34110400
H	-2.48938800	-3.20496200	2.30046900
H	-1.62014100	-4.26128000	1.20904700
H	-1.06291800	-2.60764500	1.42218100
C	-3.90647200	0.09814800	-2.09198300
H	-4.66252000	0.70796200	-1.59028300

H	-2.97970400	0.67477400	-2.08159200
H	-4.21205700	-0.02606400	-3.13520300
C	-4.78788700	-4.80864500	-2.46376800
H	-4.84962000	-4.59744600	-3.53594900
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H	-5.80996600	-4.99240300	-2.10891200
C	-0.80357500	-0.16285100	0.48020800
C	-0.17779500	-0.68214100	-0.66589200
C	0.04496800	0.39047400	1.45877600
C	1.20566400	-0.62692700	-0.84842300
H	-0.78957100	-1.13527500	-1.44018700
C	1.42988800	0.44465500	1.30135500
H	-0.37499000	0.82704400	2.36221600
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H	2.05888400	0.88636200	2.06856700
C	3.98248300	1.23180000	-0.51327200
C	4.23997300	-0.97281700	0.56601200
C	3.21035300	2.40556300	-0.54984800
C	5.32042000	1.30753300	-0.95005000
C	5.60305300	-1.10924500	0.23394600
C	3.70636600	-1.84477200	1.53034000
C	3.75795500	3.61075900	-0.99404200
H	2.17438500	2.37494300	-0.24033400
C	5.87404600	2.52421800	-1.35432300
C	6.40807200	-2.04681400	0.88432400
H	2.65884800	-1.77652700	1.79188600
C	4.50734300	-2.80746900	2.14809600
C	5.09452300	3.68275700	-1.38826500
H	3.13032900	4.49606100	-1.01942900
H	6.91348600	2.55236100	-1.66655000
C	5.86433500	-2.90892000	1.83943200
H	7.45867500	-2.11383500	0.61876100
H	4.06102000	-3.47198300	2.88129800
H	5.52666000	4.62021000	-1.72211900
H	6.49217700	-3.64763600	2.32637900
S	6.28259100	-0.17965100	-1.12296300
N	3.43632900	0.00132300	-0.07347200
N	-2.61071100	-0.56841900	2.29699800
H	-2.66834300	0.30048500	2.82695200
H	-3.46663100	-1.08359500	2.49098000
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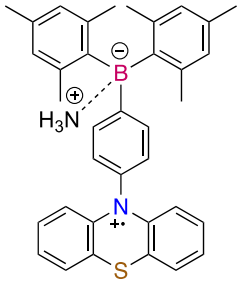
Ammonia adduct of (10-Phenylphenothiazinyl)dimesitylborane radical cation (**3$^{\bullet+}$-NH$_3$**)



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C	4.59571700	1.25466700	-1.00853100
C	3.23474200	1.21077200	-0.58911200
C	2.68592800	2.43680500	-0.11759800
C	3.44276600	3.61842400	-0.13955400
C	4.75875900	3.66130500	-0.60150800
H	6.36204100	2.43620300	-1.33186700
H	2.98941400	4.53415900	0.23446300
B	2.41475800	-0.21735300	-0.70191100
C	2.98970200	-1.46691900	0.19783300
C	2.77213900	-2.82066300	-0.18276500
C	3.65176500	-1.26449600	1.44114900
C	3.29485000	-3.88160800	0.57178800
C	4.15489000	-2.34959700	2.17408200
C	4.01880400	-3.67056500	1.74493800
H	3.11053800	-4.90177200	0.24047300
H	4.65860400	-2.15269400	3.11835400
C	5.38701600	0.02668200	-1.43431400
H	5.02795100	-0.88918000	-0.96270700
H	5.38082000	-0.11211600	-2.52387900
H	6.43731500	0.14551900	-1.15355800
C	1.30537800	2.57375400	0.49937900
H	1.09849400	1.78990500	1.23047500
H	1.22419300	3.53664400	1.01136900
H	0.50706200	2.52720100	-0.24549400
C	5.53597700	4.95412900	-0.65070500
H	6.60944000	4.77871800	-0.52997400
H	5.39451600	5.46185600	-1.61319600
H	5.21006600	5.64541600	0.13262900
C	1.92985700	-3.22970800	-1.38039400
H	2.49000300	-3.21557600	-2.32332300
H	1.57742700	-4.25662500	-1.25335500
H	1.04299100	-2.59997700	-1.49281300
C	3.82649000	0.09821500	2.08445700
H	4.60747700	0.69065900	1.60061100
H	2.91089700	0.69124700	2.04242200
H	4.09911200	-0.02223000	3.13706600
C	4.61425800	-4.81843400	2.52335400
H	4.64884800	-4.59812200	3.59483300
H	4.03958700	-5.73865700	2.37959300

H	5.64276500	-5.02196800	2.19951700
C	0.79238700	-0.14542000	-0.55404900
C	0.15413500	-0.62771100	0.60324500
C	-0.04036100	0.38286400	-1.55837600
C	-1.22728000	-0.55761800	0.77681500
H	0.75596400	-1.06225900	1.39480300
C	-1.42720700	0.45383300	-1.41951100
H	0.38990800	0.78744600	-2.47061100
C	-2.00447400	-0.01058100	-0.24131100
H	-1.69945800	-0.92014200	1.68448100
H	-2.05090000	0.87518000	-2.20145000
C	-3.93795000	1.25526700	0.50358000
C	-4.21295000	-0.99917900	-0.47605500
C	-3.04121300	2.28097200	0.88872400
C	-5.32634300	1.46722800	0.71790400
C	-5.62840400	-1.01531100	-0.35562400
C	-3.57937600	-2.13477700	-1.03534100
C	-3.50794700	3.45240100	1.45348300
H	-1.98031400	2.14390200	0.73928800
C	-5.78284900	2.66678100	1.29376600
C	-6.36602400	-2.13500500	-0.78092100
H	-2.50397700	-2.14575500	-1.13823500
C	-4.32041000	-3.22562300	-1.44791200
C	-4.88548600	3.65390300	1.65947700
H	-2.79808800	4.22060200	1.73903600
H	-6.84761400	2.80685900	1.44764400
C	-5.72221000	-3.23301800	-1.32256900
H	-7.44603900	-2.12566700	-0.67857700
H	-3.80903300	-4.08254700	-1.87193000
H	-5.24519500	4.57540200	2.10284400
H	-6.29776000	-4.09225400	-1.64747600
S	-6.55093500	0.30358000	0.30332500
N	-3.44309100	0.08547200	-0.06670700
N	2.63845800	-0.57778100	-2.33103900
H	2.70472500	0.28658200	-2.86773700
H	3.50495200	-1.08572100	-2.49654700
H	1.88717900	-1.13156400	-2.73656700

FIA reference system – COF_2

COF_2

C	0.00000000	0.00000000	0.14193800
O	0.00000000	0.00000000	1.32362300
F	0.00000000	1.07077100	-0.63559000
F	0.00000000	-1.07077100	-0.63559000

COF_3^-

C	-0.00043800	-0.00080900	0.18703200
F	0.81509500	-0.98466300	-0.46288100
F	0.44863200	1.20009900	-0.45449800

F	-1.26058000	-0.20956500	-0.46430100
O	-0.00321300	-0.00599800	1.41411600

HIA reference system – Me_3SiH

Me_3SiH

Si	0.00003700	-0.00002600	0.37851100
H	0.00000400	-0.00008800	1.87466800
C	1.78840000	-0.07510600	-0.22289700
H	1.82481900	-0.07687200	-1.31861300
H	2.36158600	0.78841500	0.13246900
H	2.28726500	-0.98340800	0.13290200
C	-0.95927900	-1.51105100	-0.22301700
H	-0.49823600	-2.43929400	0.13231100
H	-1.99535200	-1.48873700	0.13269700
H	-0.97894800	-1.54155700	-1.31871700
C	-0.82915600	1.58619400	-0.22297700
H	-1.86343900	1.65091800	0.13276200
H	-0.29181200	2.47243300	0.13240500
H	-0.84620400	1.61832600	-1.31870000

Me_3Si^+

Si	0.00000000	-0.00017000	0.00000000
C	-1.62246100	-0.86844700	0.00000000
H	-2.19877300	-0.55558800	0.88038400
H	-1.51473100	-1.95490300	0.00000000
H	-2.19877300	-0.55558800	-0.88038400
C	0.05888200	1.83894200	0.00000000
C	1.56364100	-0.97029100	0.00000000
H	0.61756200	2.18184700	0.88045300
H	1.58143200	-1.62554800	0.88043000
H	0.61756200	2.18184700	-0.88045300
H	1.58143200	-1.62554800	-0.88043000
H	-0.93631100	2.28784800	0.00000000
H	2.45022600	-0.33320900	0.00000000

AA reference system – NH_3

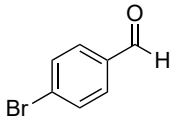
NH_3

N	0.00000000	0.00000000	0.11362800
H	0.00000000	0.94419800	-0.26513200
H	-0.81770000	-0.47209900	-0.26513200
H	0.81770000	-0.47209900	-0.26513200

S8.2 Optimized Coordinates for Mechanistic Investigation

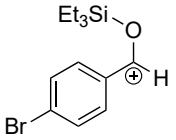
Lewis Acid Mediated Pathway:

4-Bromobenzene



C	*-0.05001100*	*1.29522200*	*0.00003900*
C	*1.34232400*	*1.36996900*	*0.00024100*
C	*2.11787300*	*0.20064000*	*0.00031400*
C	*1.48779300*	*-1.05579400*	*0.00018600*
C	*0.10016900*	*-1.14371400*	*-0.00001700*
C	*-0.65241500*	*0.03649500*	*-0.00007900*
H	*-0.65212600*	*2.19635300*	*-0.00002200*
H	*1.82743500*	*2.34226200*	*0.00034200*
H	*2.09355000*	*-1.95603400*	*0.00024600*
H	*-0.39237700*	*-2.10925900*	*-0.00012300*
C	*3.58810600*	*0.31624000*	*0.00054300*
H	*3.97764700*	*1.35250200*	*0.00061800*
O	*4.36393000*	*-0.63215400*	*0.00062500*
Br	*-2.55338900*	*-0.08237000*	*-0.00038300*

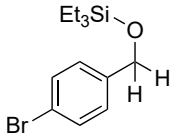
4-Bromo((triethylsiloxy)methyl)benzene cation



C	2.92922300	-1.31877700	-0.55840400
C	1.55705400	-1.49515800	-0.65347100
C	0.67905400	-0.46584600	-0.24134300
C	1.19667700	0.74922200	0.26983100
C	2.56472000	0.92674700	0.36552600
C	3.41811700	-0.10965800	-0.04951800
H	3.61003500	-2.10078800	-0.87169600
H	1.15725200	-2.42475800	-1.04606000
H	0.51850900	1.53450500	0.58392300
H	2.97605800	1.85038000	0.75452700
C	-0.72075900	-0.69400000	-0.35894000
H	-1.06649900	-1.65025900	-0.75984400
O	-1.58186700	0.17453800	-0.01490600
Br	5.28592800	0.13984500	0.08437100
Si	-3.39050100	0.14670600	-0.08307600
C	-3.85146600	0.46314900	1.70884900
H	-4.94118000	0.60636500	1.72711000
H	-3.42231500	1.43015200	2.00038100
C	-3.44462600	-0.62604400	2.71996500
H	-2.35814700	-0.75709500	2.75723200

H	-3.77659800	-0.35854200	3.72862000
H	-3.88935700	-1.59582600	2.47434000
C	-3.85715500	-1.54756100	-0.75145300
H	-3.41182700	-1.66931300	-1.74734400
H	-3.41324100	-2.32306400	-0.11408600
C	-5.38364100	-1.77466800	-0.84377900
H	-5.59690700	-2.77230600	-1.24054400
H	-5.86542900	-1.70099500	0.13656100
H	-5.86275600	-1.04769100	-1.50743800
C	-3.76989800	1.56335300	-1.25432900
H	-3.34820500	1.30337400	-2.23409800
H	-4.86029100	1.56889100	-1.39203100
C	-3.28923200	2.96100500	-0.81777300
H	-2.20163500	2.99394300	-0.69760700
H	-3.56168800	3.71265700	-1.56605200
H	-3.73972100	3.26503500	0.13246500

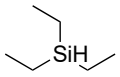
4-Bromo((triethylsiloxy)methyl)benzene



C	-3.02465500	-1.38896300	-0.30881400
C	-1.65559800	-1.63759200	-0.40908800
C	-0.71632100	-0.62040900	-0.18323700
C	-1.17383500	0.66023200	0.14056900
C	-2.54351200	0.92865700	0.24291600
C	-3.45259500	-0.10098700	0.01666400
H	-3.74172900	-2.18319600	-0.48429400
H	-1.31965600	-2.63937800	-0.66599100
H	-0.45434200	1.45260300	0.31247300
H	-2.88825900	1.92569800	0.49442800
C	0.76147500	-0.94111000	-0.29496500
H	1.01941600	-1.68731200	0.47158500
O	1.55399400	0.22417400	-0.14988400
Br	-5.33127000	0.25343600	0.15752900
Si	3.23476300	0.25901600	0.07640500
C	4.12938200	-0.67789700	-1.31177700
H	5.17071600	-0.32378000	-1.30990800
H	3.71023600	-0.34178600	-2.27029100
C	4.11715800	-2.21848800	-1.24782600
H	3.10140500	-2.62318400	-1.30853700
H	4.68929300	-2.65464800	-2.07511900
H	4.55951400	-2.58735400	-0.31600300
C	3.63500300	-0.47921800	1.77681000
H	3.05634800	0.08126500	2.52415000
H	3.25284600	-1.50861500	1.81524200
C	5.12869400	-0.47194200	2.16163200
H	5.28759300	-0.91142300	3.15319600
H	5.73329300	-1.04607900	1.45049000

H	5.53361200	0.54585900	2.18775800
C	3.65726900	2.09972400	0.02375800
H	3.09655600	2.59007800	0.83186100
H	4.71806300	2.20795200	0.28986500
C	3.38227300	2.81644300	-1.31240100
H	2.32522200	2.75017400	-1.59139300
H	3.64192100	3.88015100	-1.25593100
H	3.96659700	2.38141400	-2.13095200
H	0.94875800	-1.40900800	-1.27217100

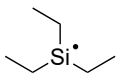
Triethylsilane



Si	0.02286100	-0.26131800	0.73338400
H	0.45027700	-0.68690300	2.10668400
C	-1.78259200	-0.83010800	0.53420400
H	-1.81302700	-1.88693800	0.83557300
H	-2.38591400	-0.29374000	1.28010800
C	1.15017700	-1.13540900	-0.52331800
H	0.84645900	-0.83859600	-1.53656500
H	0.94874800	-2.21377700	-0.45680500
C	0.23922400	1.62951700	0.67221200
H	-0.45859200	2.06727900	1.39989600
H	1.24348500	1.84946100	1.06088800
C	-2.42132400	-0.67836800	-0.85996700
H	-1.85192900	-1.21680000	-1.62593700
H	-3.44347100	-1.07538600	-0.87485400
H	-2.47619000	0.37051500	-1.17006500
C	2.65692800	-0.87495600	-0.33523400
H	3.25546100	-1.42037500	-1.07473000
H	2.89895700	0.18871600	-0.44090100
H	2.99656400	-1.19014300	0.65828800
C	0.06111100	2.31109600	-0.69819300
H	0.24938500	3.38955300	-0.63427500
H	0.75247500	1.90379200	-1.44466800
H	-0.95387800	2.18118000	-1.08823600

Hydrogen Atom Transfer (HAT) Mediated Pathway:

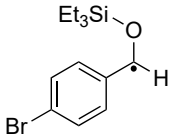
Triethylsilyl radical



Si	-0.01204400	-0.23930400	-0.77917500
C	1.81226300	-0.77676700	-0.58158700
H	1.88988100	-1.80617600	-0.95687300
H	2.41574500	-0.16398100	-1.26455000
C	-1.13913200	-1.18200400	0.44126200
H	-0.84574200	-0.89864300	1.46379400
H	-0.90850800	-2.25183700	0.35029700

C	-0.26730700	1.65309800	-0.66567100
H	0.44361900	2.12479700	-1.35717600
H	-1.26463500	1.87672600	-1.06721200
C	2.40294100	-0.70932100	0.84412400
H	1.83334800	-1.32814700	1.54594200
H	3.43966900	-1.06867600	0.85751300
H	2.40640900	0.31368600	1.23417800
C	-2.64993600	-0.95257100	0.25396500
H	-3.23526300	-1.51791600	0.98903300
H	-2.91498200	0.10451700	0.36938000
H	-2.98098800	-1.26565400	-0.74287100
C	-0.12945100	2.28177700	0.73840500
H	-0.33221300	3.35978200	0.70845400
H	-0.83262100	1.83673500	1.45097000
H	0.87862700	2.14976400	1.14458200

4-Bromo((triethylsiloxy)methyl)benzyl radical



C	2.93438600	-1.39227700	-0.25174700
C	1.56449900	-1.59434300	-0.31292100
C	0.64860800	-0.50645900	-0.18928900
C	1.19195000	0.79974200	-0.00231700
C	2.56483000	1.00065000	0.05802000
C	3.42995300	-0.09292600	-0.06753600
H	3.61499600	-2.23140200	-0.34698300
H	1.18037900	-2.60063900	-0.45668500
H	0.51904500	1.64468700	0.09367500
H	2.96278700	1.99978500	0.20067300
C	-0.73932200	-0.74469000	-0.25929800
H	-1.12692700	-1.74912000	-0.40944300
O	-1.61803100	0.27279600	-0.16106200
Br	5.32175900	0.18665600	0.01653000
Si	-3.33600100	0.18381100	-0.07569000
C	-3.81468400	-0.15557100	1.72150300
H	-4.91197100	-0.11210300	1.77855700
H	-3.45411200	0.68455900	2.32991300
C	-3.31274800	-1.48441100	2.31896800
H	-2.21848500	-1.53705500	2.31948800
H	-3.64557100	-1.60326400	3.35644700
H	-3.68362300	-2.34801200	1.75593700
C	-3.91552000	-1.18212800	-1.24926900
H	-3.49816000	-0.97104900	-2.24326800
H	-3.47642000	-2.13839200	-0.93545800
C	-5.44798800	-1.33418800	-1.34796200
H	-5.72027100	-2.13817800	-2.04082700
H	-5.89418400	-1.57529500	-0.37679600
H	-5.92341500	-0.41616500	-1.71021100

C	-3.90390700	1.88900200	-0.64442100
H	-3.61813200	1.99748700	-1.69977100
H	-5.00276500	1.89340800	-0.63134900
C	-3.36985300	3.08469100	0.16842200
H	-2.27560200	3.12323000	0.15128300
H	-3.73972000	4.03401400	-0.23558200
H	-3.68238900	3.03226800	1.21706100

S9 Single Crystal X-Ray Diffraction

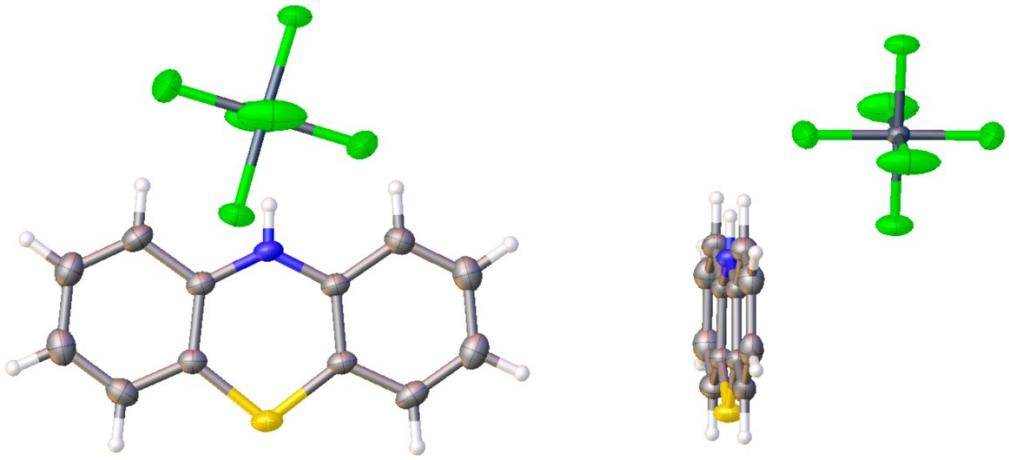


***Figure S22**: Solid state structure of **1**$^{\bullet+}$; a) front view and b) side view. Thermal ellipsoids are drawn at 50 % probability. N: Blue, S: Yellow, F: Green, Sb: Dark Grey, C: Light Grey.*

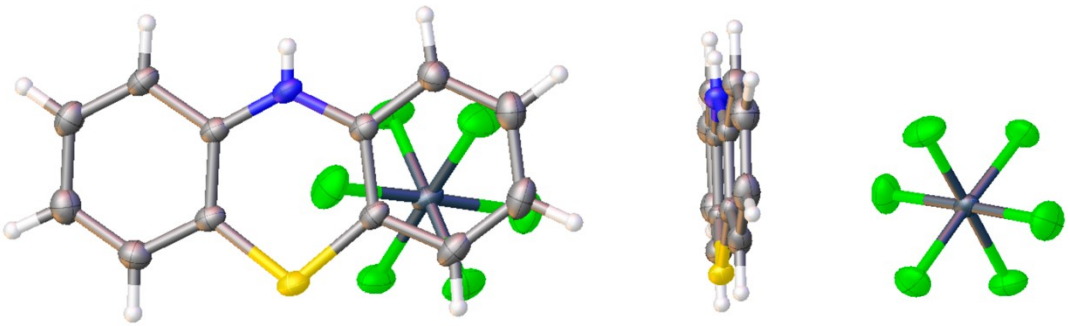


***Figure S23**: Solid state structure of **2**$^{\bullet+}$; a) front view and b) side view. Thermal ellipsoids are drawn at 50 % probability. N: Blue, S: Yellow, F: Green, Sb: Dark Grey, C: Light Grey.*

***Table 3**: Crystal data and structure refinement for **1**$^{\bullet+}$ and **2**$^{\bullet+}$.*

Molecule	**1**$^{\bullet+}$	**2**$^{\bullet+}$
Formula	$C_{12}H_9F_6NSSb$	$C_{12}H_9F_6NSSb$
Formula wt (gmol^{-1})	435.01	435.01
Temperature (K)	173.0	173.0
Crystal System	Monoclinic	Triclinic
Space Group	P21/m	P-1
a/Å	8.2631(2)	8.1743(3)
b/Å	6.6836(2)	8.4346(3)
c/Å	13.0719(3)	10.2616(4)
α/°	90	90.700(2)
β/°	96.1440(10)	104.821(2)
γ/°	90	93.8490(10)
Volume/Å^3	717.78(3)	682.11(4)
Z	2	2
ρcalc g/cm^3	2.013	2.118
μ/mm^{-1}	2.124	2.235
F(000)	418.0	418.0

Crystal size/mm^3	0.1 × 0.1 × 0.01	0.2 × 0.2 × 0.02
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.958 to 72.926	4.108 to 72.636
Index ranges	-13 ≤ h ≤ 13, -11 ≤ k ≤ 11, -21 ≤ l ≤ 21	--13 ≤ h ≤ 13, -14 ≤ k ≤ 14, -17 ≤ l ≤ 17
Reflections collected	40310	62268
Independent reflections	3739 [R_{int} = 0.0525, R_{sigma} = 0.0275]	6606 [R_{int} = 0.0413, R_{sigma} = 0.0206]
Data/restraints/parameters	3739/0/127	6606/0/226
Goodness-of-fit on F^2	1.086	1.123
Final R indexes [I>=2σ (I)]	R_1 = 0.0326, wR_2 = 0.0613	R_1 = 0.0248, wR_2 = 0.0487
Final R indexes [all data]	R_1 = 0.0437, wR_2 = 0.0650	R_1 = 0.0355, wR_2 = 0.0549
Largest diff. peak/hole / e Å^{-3}	0.77/-0.89	1.20/-0.72

Table S4: Bond lengths for 1$^{\bullet+}$.

Atom	**Atom**	**Length/Å**
Sb1	F1	1.852(2)
Sb1	F2^1	1.8640(16)
Sb1	F2	1.8640(16)
Sb1	F3	1.8735(16)
Sb1	F4	1.8736(15)
Sb1	F5	1.852(2)
S1	C3	1.725(3)
S1	C9	1.730(3)
N1	C4	1.364(3)
N1	C5	1.364(3)
C1	C2	1.373(4)
C1	C11	1.403(4)
C2	C3	1.403(4)
C3	C4	1.411(3)
C4	C12	1.418(4)
C5	C6	1.419(4)
C5	C9	1.413(3)
C6	C7	1.359(4)
C7	C8	1.406(5)
C8	C10	1.375(4)
C9	C10	1.394(4)
C11	C12	1.363(4)

^{1}+X,3/2-Y,+Z

Table S5: Bond angles for 1$^{\bullet+}$.

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
F1	Sb1	F2	89.18(7)	C2	C3	S1	117.65(19)
F1	Sb1	F2^1	89.18(7)	C2	C3	C4	119.5(2)
F1	Sb1	F3	88.90(9)	C4	C3	S1	122.9(2)
F1	Sb1	F4	89.75(9)	N1	C4	C3	121.7(2)
F2	Sb1	F2^1	178.34(13)	N1	C4	C12	118.8(2)
F2	Sb1	F3	89.84(5)	C3	C4	C12	119.5(2)
F2^1	Sb1	F3	89.84(5)	N1	C5	C6	118.4(2)
F2	Sb1	F4	90.14(5)	N1	C5	C9	122.0(2)
F2^1	Sb1	F4	90.14(5)	C9	C5	C6	119.5(2)
F3	Sb1	F4	178.65(8)	C7	C6	C5	119.4(3)

F5	Sb1	F1	179.86(9)	C6	C7	C8	120.9(3)
F5	Sb1	F2	90.82(7)	C10	C8	C7	120.6(3)
F5	Sb1	F2[1]	90.82(7)	C5	C9	S1	122.4(2)
F5	Sb1	F3	90.96(9)	C10	C9	S1	117.9(2)
F5	Sb1	F4	90.39(9)	C10	C9	C5	119.8(2)
C3	S1	C9	103.69(12)	C8	C10	C9	119.8(3)
C4	N1	C5	127.3(2)	C12	C11	C1	121.3(3)
C2	C1	C11	120.1(3)	C11	C12	C4	119.5(3)
C1	C2	C3	120.3(3)				

Table S6: Bond lengths for 2$^{\bullet+}$.

Atom	**Atom**	**Length/Å**
Sb1	F1	1.8681(12)
Sb1	F2	1.8664(12)
Sb1	F3	1.8619(10)
Sb1	F4	1.8886(11)
Sb1	F5	1.8799(10)
Sb1	F6	1.8706(12)
S1	C3	1.7257(15)
S1	C10	1.7209(17)
C3	C4	1.413(2)
C3	C5	1.401(2)
C4	C6	1.412(2)
C4	N	1.380(2)
C10	C7	1.409(2)
C10	C11	1.406(2)
C7	C12	1.411(2)
C7	N	1.370(2)
C6	C8	1.372(3)
C5	C9	1.374(3)
C12	C13	1.373(3)
C11	C14	1.376(3)
C8	C9	1.404(3)
C14	C13	1.397(3)

Table S7: Bond angles for 2$^{\bullet+}$.

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
F1	Sb1	F4	178.54(5)	C6	C4	C3	119.48(15)
F1	Sb1	F5	90.20(6)	N	C4	C3	121.93(13)
F1	Sb1	F6	91.33(6)	N	C4	C6	118.58(14)
F2	Sb1	F1	89.67(7)	C7	C10	S1	123.32(12)
F2	Sb1	F4	90.56(6)	C11	C10	S1	117.52(13)
F2	Sb1	F5	90.46(6)	C11	C10	C7	119.16(16)

F2	Sb1	F6	178.50(6)	C10	C7	C12	119.83(15)
F3	Sb1	F1	91.62(6)	N	C7	C10	121.85(15)
F3	Sb1	F2	90.17(6)	N	C7	C12	118.31(14)
F3	Sb1	F4	89.82(5)	C8	C6	C4	119.88(15)
F3	Sb1	F5	178.07(5)	C9	C5	C3	120.25(16)
F3	Sb1	F6	90.91(6)	C13	C12	C7	119.55(17)
F5	Sb1	F4	88.35(5)	C14	C11	C10	120.28(17)
F6	Sb1	F4	88.40(6)	C6	C8	C9	120.52(16)
F6	Sb1	F5	88.42(6)	C5	C9	C8	120.41(17)
C10	S1	C3	103.35(7)	C11	C14	C13	120.23(17)
C4	C3	S1	122.75(12)	C12	C13	C14	120.95(18)
C5	C3	S1	117.81(12)	C7	N	C4	126.07(13)
C5	C3	C4	119.43(14)				

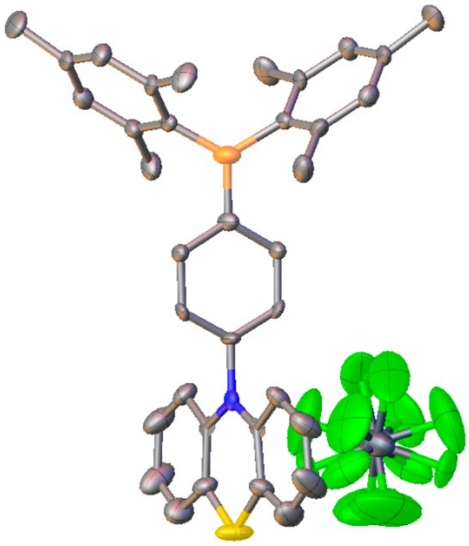


***Figure S24**: Solid state structure of **3**$^{\bullet+}$. Thermal ellipsoids are drawn at 50 % probability and hydrogen atoms are omitted for clarity. N: Blue, S: Yellow, F: Green, Sb: Dark Grey, C: Light Grey, B: Orange.*

***Table S8**: Crystal data and structure refinement for **3**$^{\bullet+}$.*

Molecule	**3**$^{\bullet+}$
Formula	$C_{36}H_{34}BF_{7.07}NSSb_{1.12}$
CCDC ID	2335095
Formula wt (gmol^{-1})	793.85
Temperature (K)	173.0
Crystal System	Orthorhombic
Space Group	Pccn
a/Å	8.8901(3)
b/Å	16.4785(6)
c/Å	27.2684(9)
α/°	90
β/°	90

γ/°	90
Volume/Å^3	3994.7(2)
Z	4
ρcalc g/cm^3	1.320
μ/mm^{-1}	0.877
F(000)	1594.0
Crystal size/mm^3	0.2 × 0.075 × 0.075
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.878 to 53.074
Index ranges	-11 ≤ h ≤ 11, -20 ≤ k ≤ 20, -34 ≤ l ≤ 34
Reflections collected	92047
Independent reflections	4156 [R_{int} = 0.0481, R_{sigma} = 0.0168]
Data/restraints/parameters	4156/0/286
Goodness-of-fit on F^2	1.134
Final R indexes [I>=2σ (I)]	R1 = 0.0968, wR2 = 0.2120
Final R indexes [all data]	R1 = 0.1024, wR2 = 0.2151
Largest diff. peak/hole / e Å^{-3}	0.84/-0.77

Table S9: Bond lengths for 3$^{\bullet+}$.

Atom	**Atom**	**Length/Å**
Sb01	F1	1.868(12)
Sb01	F11	1.868(12)
Sb01	F3	1.812(14)
Sb01	F31	1.812(14)
Sb01	F4	1.815(14)
Sb01	F41	1.815(13)
S	C00L	1.726(8)
S	C00L2	1.726(8)
C005	N006	1.393(8)
C005	C00C	1.400(11)
C005	C00L	1.422(9)
N006	C00H	1.457(11)
C007	C009	1.400(11)
C007	C00I	1.370(12)
C007	C00J	1.480(10)
C008	C00O	1.418(8)
C008	C00O2	1.418(8)
C008	B00P	1.574(14)
C009	C00E	1.402(10)
C00A	C00E	1.408(11)
C00A	C00F	1.410(10)
C00A	B00P	1.586(8)
C00B	C00H	1.373(8)
C00B	C00O	1.393(9)
C00C	C00D	1.366(14)
C00D	C00G	1.383(16)
C00E	C00M	1.553(11)

C00F	C00I	1.392(10)
C00F	C00N	1.498(12)
C00G	C00K	1.341(15)
C00K	C00L	1.387(12)
Sb1	Sb11	0.43(9)
Sb1	F2	1.77(5)
Sb1	F21	1.85(5)
Sb1	F7	1.73(3)
Sb1	F71	1.92(3)
Sb1	F9	1.62(4)
Sb1	F91	2.00(5)
F7	F71	1.77(7)

Table S10: Bond angles for 3$^{\bullet+}$.

Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
F1	Sb01	F11	148(2)	C00D	C00C	C005	119.8(8)
F3	Sb01	F1	91.5(10)	C00C	C00D	C00G	121.7(10)
F3	Sb01	F11	79.5(8)	C009	C00E	C00A	120.5(7)
F31	Sb01	F1	79.5(8)	C009	C00E	C00M	117.5(7)
F31	Sb01	F11	91.5(10)	C00A	C00E	C00M	121.9(7)
F31	Sb01	F3	148(2)	C00A	C00F	C00N	122.4(6)
F3	Sb01	F41	117.3(12)	C00I	C00F	C00A	118.7(7)
F3	Sb01	F4	90.7(12)	C00I	C00F	C00N	118.9(7)
F31	Sb01	F4	117.3(12)	C00K	C00G	C00D	120.0(10)
F31	Sb01	F41	90.7(12)	C00B	C00H	N006	118.8(4)
F41	Sb01	F11	78.4(13)	C00B2	C00H	N006	118.8(4)
F41	Sb01	F1	132.1(13)	C00B	C00H	C00B2	122.5(9)
F4	Sb01	F1	78.4(13)	C007	C00I	C00F	124.2(8)
F4	Sb01	F11	132.1(13)	C00G	C00K	C00L	120.5(9)
F41	Sb01	F4	64.9(13)	C005	C00L	S	123.7(6)
C00L2	S	C00L	103.2(5)	C00K	C00L	S	115.9(6)
N006	C005	C00C	120.4(6)	C00K	C00L	C005	120.4(8)
N006	C005	C00L	122.1(7)	C00B	C00O	C008	119.4(6)
C00C	C005	C00L	117.4(7)	C008	B00P	C00A2	119.9(4)
C005	N006	C0052	125.1(8)	C008	B00P	C00A	119.9(4)
C005	N006	C00H	117.4(4)	C00A2	B00P	C00A	120.2(8)
C0052	N006	C00H	117.4(4)	Sb11	Sb1	F2	95(10)
C009	C007	C00J	120.9(8)	Sb11	Sb1	F7	110(3)
C00I	C007	C009	117.1(7)	Sb11	Sb1	F91	26(9)
C00I	C007	C00J	121.8(8)	Sb11	Sb1	F9	148(10)
C00O	C008	C00O2	119.4(8)	F2	Sb1	F91	71.0(17)
C00O	C008	B00P	120.3(4)	F21	Sb1	F91	85(2)

C00O2	C008	B00P	120.3(4)	F7	Sb1	F2	95(3)
C007	C009	C00E	121.2(7)	F7	Sb1	F91	120(2)
C00E	C00A	C00F	118.5(6)	F71	Sb1	F91	80(2)
C00E	C00A	B00P	120.2(6)	F9	Sb1	F2	100(3)
C00F	C00A	B00P	121.2(6)	F9	Sb1	F7	97(3)
C00H	C00B	C00O	119.6(7)	F9	Sb1	F91	142(2)

S10 References

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